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EFFECT OF pH ON ELECTRIC CHARGES CARRIED BY CLAY PARTICLES

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THE work described in this paper was undertaken mainly in the hope of elucidating the phenomenon of soil acidity. In one of the first quantitative studies of soil acidity Veitch [1] showed that, whether measured by his lime-water method [2] or by extraction with normal sodium chloride [3], there are many mineral soils which exhibit large 'lime requirements'. Veitch drew attention to the presence of aluminium as chloride in the N.NaCl extracts, and its precipitation as hydroxide when the extract is titrated with alkali. He suggested that the aluminium is brought into solution by base exchange.

It has been difficult to be sure of what happens when alkali is added to an acid soil. Bradfield [4] titrated solutions of $Ca(OH)_2$ and NaOH with 1 per cent. suspension of clay fractions from four very acid mineral soils. He observed that the pH changed in the same general way as in the titration of a weak acid. He also found [5] that the rise in pH on diluting suspensions of acid clays closely resembled that observed on diluting a weak acid such as acetic acid. If the interpretation favoured by Bradfield is correct, the hydroxyl ions of the added alkali react with hydrions that dissociate from the 'clay acid'. An alternative possibility suggested by the observations of Veitch is that the added hydroxyl ions combine with exchangeable aluminium ions.

The observation of Mattson [6] that certain soils, when acid, can retain anions such as chloride led him to conclude that soil colloids may also exhibit a weak basic character. The exact significance of this observation has been somewhat obscured in subsequent discussions by Mattson and his collaborators [7], who have represented the interaction as an exchange of OH ions for other anions, whereas it seems more likely to be a proton transfer (see below).

Interest in the role played by aluminium was revived by the work of Paver and Marshall [8], who observed that aluminium-chloride solutions do not react with acid-washed clays. They concluded that the liberation of aluminium from unsaturated clays by neutral salt solutions is due to direct exchange, and that unsaturated clays are to be regarded as mixed aluminium-hydrogen clays rather than pure hydrogen clays.

No really satisfactory way has yet been devised for disentangling the contributions made by 'clay acids' on the one hand and exchangeable aluminium on the other to buffer action of clay between pH 3 and pH 6. Consequently it has not been possible to disprove the existence of clay acids comparable in acid strength to acetic acid. Nevertheless this conception encounters the serious obstacle that no chemical grouping in which oxygen and hydrogen are combined with silicon or aluminium, or both, is known which has a weak acid character comparable with the carboxyl group. It was formerly thought that colloids might exhibit buffering in consequence of non-specific 'physical adsorption' of hydrogen

or hydroxyl ions at their surfaces, but this view has now few, if any, adherents. Saric and Schofield [9] measured the degree of dissociation of the carboxyl groups in samples of fibre, cellulose, hemicellulose, xylan, alginic acid, arabic acid, and pectic acid. During titration these polysaccharides were suspended or dissolved in N.KCl solution, the object being to make the radius of the ionic atmosphere smaller than the least distance separating carboxyl groups. In general it was found that the dissociation of these carboxyl groups was governed by the same dissociation constant (pK = 2·95) regardless of whether they were part of a molecule in solution or sol (arabic acid, alginic acid) or part of a molecule built into semi-crystalline fibres (cellulose) or into amorphous particles (precipitated hemicellulose and xylan). A peculiar behaviour exhibited by pectic acid was attributed to the formation of hydrogen bridges between pairs of carboxyl groups. This work showed that the buffer action of a solid in suspension can be precisely matched by that of a substance in solution carrying the same type of acid group provided that the comparison is made in a strong solution of a neutral salt.

Previous to this investigation a study, using a similar technique, was made [10] of the buffer action of several clays: 5-gm. samples were shaken overnight with 50 c.c. of N.KCl containing graded amounts of HCl in centrifuge tubes. The pH values were determined, the tubes were centrifuged, and 25 c.c. of each clear extract was titrated with KOH to pH 6 using bromo cresol purple as indicator. The clay samples were then shaken up in the remaining 25 c.c., and the suspensions were each titrated to pH 6, additional drops of alkali being added from time to time until the pH became steady. The excess of the titre of the remainder over that of the extract evidently gave the alkali that had reacted with each sample of clay in taking it from the pH first measured to pH 6. The outstanding feature of the results obtained in this way was the smallness of the buffering due to the clay itself compared with its base-exchange capacity. Indeed, between pH 2 and pH 5 hardly any buffering was found except with red and brown soil clays of undetermined mineralogical composition that exhibited the ability to retain chloride ions when suspended in HCl solutions. The ability to retain chloride is evidence of a weak basic character which, as will be shown, appears to be the property of an iron incrustation on the particles of clay mineral and not a property of the clay mineral proper.

While the results of this investigation seemed to show beyond question that the clays investigated do not exhibit a weak acid character in the range pH 2–pH 6, the technique employed was not entirely satisfactory inasmuch as the titre found for the clay depended to some extent on the time allowed. In view of the fundamental nature of the inquiry, it was obviously desirable to eliminate experimental uncertainties as far as possible. A new experimental procedure was therefore devised which measures directly the net electric charge carried by the clay when suspended in solutions of known pH and salt concentration.

Measurement of Net Electric Charge on Clay

The fundamental notion underlying the method employed is that the excess of the free and exchangeable cations in the system over the free

and exchangeable anions must give the net negative charge carried by the clay. The underlying idea will be made clear by describing the essential features of the experimental procedure. A sample (say, 5 gm.) of the clay is placed in a 100-c.c. centrifuge tube and 50 c.c. of a solution N/5 in NH_4Cl and N/1000 in HCl is added. The tube is well shaken, centrifuged, and the clear solution poured or sucked off so as to avoid as far as possible the loss of any clay. Another 50 c.c. of the solution is added and the process is repeated until the clay appears to have been brought to equilibrium with it.

Three tests are applied to the solution that is poured off in order to decide whether a state of equilibrium has been reached. In the first place it should be free from the cations (e.g. calcium) originally exchangeable in the clay. Secondly, the concentration of free aluminium which at first tends to rise as the pH falls, should again have fallen to what appears to be an irreducible minimum. Thirdly, the pH should have fallen almost to that of the solution used (e.g. pH 3). Sometimes as many as twenty washings must be given, but the author considers it essential to the success of the method that no pains be spared to reduce the concentration of free aluminium to the irreducible minimum. Aluminium ions, being trivalent, must be strongly attracted to the negative charges of the clay, and it is just as important to get rid of them as other cations such as calcium. Unfortunately it appears to be impossible to prevent the release of traces of free aluminium ions in solutions as acid as pH 3 however long the washing is continued.

When the washing with acid NH_4Cl is judged to have been sufficient, the clay is washed five times with 50-c.c. portions of N/5 KNO_3. These five washings are bulked and titrated to pH 6 and then analysed for NH_4^+ and Cl^-. To get the net negative charge, the free H_3O^+ ions must also be taken into account. Titration of the combined KNO_3 washings with alkali will not necessarily give the free H_3O^+ ions originally present, since some may have been produced by proton transfer owing to the rise in pH that occurred during the washings. The quantity of free H_3O^+ originally present was, therefore, computed by assuming that the proportion of H_3O^+ ions to NH_4^+ ions was originally the same as in the NH_4Cl solution (e.g. 1:200).

By conducting a series of experiments, in each of which the pH of the N/5 NH_4Cl solution was adjusted to a different value by the addition of suitable amounts of HCl or NH_3, the dependence of the net electric charge on pH was determined. Preliminary trials indicated that slightly higher and more reproducible results were obtained for the higher pH values if the clay were first washed with a solution at pH 3. It seems that some of the exchangeable ions originally present were more readily dislodged and replaced by NH_4 when this procedure was adopted. At the higher pH values allowance must be made for the NH_3 present in the NH_4Cl solution.

The results of a series of measurements made in this way on a sample of clay subsoil, practically devoid of organic matter, taken at a depth of 2 ft. from the Meteorological Enclosure at Rothamsted are set out in the upper part of Table 1. The net charge is expressed as milli-equivalents

per 100 gm. of oven-dry subsoil. A precise determination of the amount of clay mineral present is difficult, but it is roughly 60 per cent. of the total, and has been identified by Dr. D. M. C. MacEwan as being mainly of the illite type.

The outstanding feature of these results is the smallness of the decrease in the net charge between pH 7 and pH 2·5. This corresponds to the smallness of the buffering found by titration in the presence of N. KCl. The net negative charge only changes by 3 to 4 m.e. over this pH range.

On washing this subsoil clay with N/5 NH_4Cl containing N/100 HCl (pH 2) a net charge of only 21·5 m.e. was found. On washing other samples first with this solution and then with solutions of higher pH, lower values were obtained than when the first washings were made at pH 2·5 or pH 3. Evidently the solution at pH 2 attacks some of the clay mineral and irreversibly reduces the net charge. On the other hand, the close agreement between the results obtained at pH 2·5 and at pH 3·3 is taken as good evidence that these solutions cause no appreciable destruction of the clay minerals present in this subsoil.

Chloride Adsorption due to Basic Groups

In order that a measure might be obtained of the amount of chloride adsorbed by the clay from N/5 NH_4Cl at the different pH values employed, the centrifuge tubes were weighed empty and also just before the washings with KNO_3 solution when they contained the subsoil samples and the entrained NH_4Cl solution. Knowing the weight of oven-dry subsoil, a calculation was made of the chloride that would have been present if the ratio of water to chloride were the same as in the original NH_4Cl solution. Below pH 5 the chloride actually present exceeded the amount calculated, indicating positive adsorption of chloride, whereas above pH 6 the reverse was the case, indicating negative adsorption.

The 'calculated' amount of chloride will be too little if water not driven off in the oven is capable of dissolving chloride, and too great if oven drying removes some water not capable of dissolving chloride. Thus the zero from which the adsorption of chloride should be calculated is somewhat uncertain. It appears safe, however, to assume that the zero will not vary with pH. Hence the change of adsorption with pH will be correctly given even though the absolute amount is uncertain.

We have already seen that the rise in hydrion concentration corresponding to a fall from pH 7 to pH 2·5 causes a fall in the net negative charge on the clay. No doubt this is due to the transfer of protons to certain atom groups on the particles. We could not decide on this evidence alone whether the net negative charge had decreased because some of the negatively charged groups had become uncharged (as occurs in the reaction $-COO^- + H^+ \rightarrow COOH$) or because some uncharged groups had become positively charged (as in the reaction $-NH_2 + H^+ \rightarrow -NH_3^+$).

The observed change in chloride-ion adsorption helps us here. If only negative charges were present the chloride ions would be repelled from the surfaces of the particles and the adsorption would be negative. Moreover, as the author has pointed out [11], the negative adsorption

tends towards a limiting value as the negative charge increases, and is hardly affected by changes in the negative charge when this is large. It is quite clear that a drop in the negative charge from 26 to 23 m.e. would scarcely alter the chloride adsorption. On the other hand, the development of some 3 m.e. of positive charges would produce an effect of this magnitude provided that they are separated from the negative charges by distances sufficiently large in comparison with the radius of the ionic atmosphere which diminishes with increase in electrolyte concentration. It is fortunate that N/5 is a high enough concentration to secure this effect, yet not too high for accurate measurement of chloride adsorption.

TABLE I

Electric Charges on a Sample of Subsoil Clay

pH	*Excess* NH_4^+ *over* Cl′ *held* m.e.*	Cl′ *adsorbed* m.e.*	*Negative charges* m.e.*	*Positive charges* m.e.*
Samples not treated with acid ammonium oxalate				
2·05	19·5	1·5	21·5	2·0
2·3	21·3	1·3	23·1	1·8
2·6	21·7	1·2	23·4	1·7
3·1	21·6	1·2	23·3	1·7
3·3	21·7	1·1	23·3	1·6
3·8	22·3	0·6	23·4	1·1
5·5	24·0	0·0	24·5	0·5
6·2	25·7	−0·4	25·7	..
7·15	27·0	−0·6	27·0	..
7·4	28·2	−0·5	28·2	..
Samples treated with acid ammonium oxalate				
2·5	23·2	−0·3	23·2	..
3·65	23·5	−0·5	23·5	..
4·15	23·3	−0·6	23·3	..
7·5	26·8	−0·4	26·8	..

* Milli-equivalents per 100 gm. of oven-dried subsoil (original weight in case of oxalate-treated samples).

We may safely conclude that most or all of the change in net charge from pH 6 to pH 2·5 is due to the development of positive charges and that little or none is due to a decrease in the numerous negative charges. From pH 6 to pH 7·5, on the other hand, there is no change in the chloride adsorption, indicating that the rise in net negative charge is due to an increase in the number of negative charges.

Treatment with Acid Oxalate

A set of samples of the same subsoil was given preliminary washings with a solution of N/5 ammonium oxalate which had been acidified to pH 3·5 by the addition of oxalic acid. The subsoil samples were first treated with neutral NH_4Cl to remove exchangeable calcium, and it was thought that by using an acid that forms a complex with aluminium the concentration of free aluminium would be greatly reduced and its

removal thus facilitated. It was noticed, however, that when the samples were shaken with the acid oxalate solution in sunlight considerable amounts of iron were brought into solution and so removed. It was found that the samples could be bleached almost white in this way, the rate of reaction depending on the amount of sunlight available. This acid oxalate solution was almost the same as that in which Tamm [12] shakes soil samples for a few hours only in order to determine the readily soluble iron and aluminium. Even in favourable weather a fortnight was required for completion of the reaction that occurred in sunlight, a fresh 50-c.c. lot of the solution being applied each day.

Measurements of the net negative charge and of the chloride adsorption were then made on the oxalate-treated samples, each of which originally weighed 5 gm. The dry weight was also found at the conclusion of the measurements, and these values were used in calculating the chloride adsorption. The results are set out in the lower part of Table 1. It will be seen that at pH 3 the net negative charge of the oxalate-treated samples is 2 m.e. greater than that of the untreated samples, the values in both cases being for 100 gm. of the untreated oven-dry material. At the same time the chloride adsorption of the treated samples has the same negative value at pH 3 as at pH 7. These results can only mean that with the 7 per cent. of dry weight dissolved away by the oxalate have gone those atom groups present in the original material which at pH 6 were uncharged, but which at pH 3 had acquired positive charges by proton transfer. The negative charge carried by the original material on the acid side of pH 6 has remained unaffected by the oxalate treatment.

Conclusions

The subsoil clay investigated contains two distinct materials on which electric charges are carried. One of these is dissolved by the acid ammonium-oxalate solution while the other is not.

Aluminium as well as iron is carried into solution in the acid ammonium-oxalate solution, but there is an indication that the positive charges developed at low pH values belong to the ferric oxide rather than to the alumina. This indication is obtained from the fact that washing with dilute HCl brings relatively more aluminium into solution, but is relatively ineffective in reducing the positive charges.

The maximum positive charge developed at low pH values is about 3 m.e. per 100 gm. of original subsoil and about 60 m.e. per 100 gm. of ferric oxide dissolved by the acid oxalate solution. This means one positive charge per 10 Fe_2O_3. The reaction that gives rise to a positive charge must be the transfer of a proton from an H_3O^+ ion to an oxygen of the hydrous ferric oxide. An oxygen capable of accepting an additional proton might occur at the edge of a regular crystal or as a result of imperfect crystallization.

The negative charges which remain at low pH values on the residue after acid-oxalate treatment may safely be attributed to the clay mineral. This conclusion is fully supported by measurements made after separation by sedimentation. Nearly all the negative charges were found on the particles $< 2\mu$ which consisted almost entirely of clay mineral, the

exchange capacity of this fraction being about 40 m.e. per 100 gm. The point to be emphasized is the persistence of the exchange capacity down to pH 2·5. This observation is in accord with the view that the negative charges arise from isomorphous replacements within the crystal lattice of the clay mineral. Such replacement is a *permanent* feature of the crystals inasmuch as it could not change *reversibly* with changes in pH.

In the absence of material that acquires positive charges at low pH values, the permanent negative charge due to isomorphous replacement can be identified with the constant negative charge found between certain limits of pH. In the case of the oxalate-treated Rothamsted subsoil these limits are pH 2·5 to pH 5. The lower limit is set by the susceptibility of the clay mineral to attack by acid, while above the upper limit additional negative charges develop in consequence of proton transfer (see below). The pH limits within which the negative charge is constant will not necessarily be exactly the same for all clay minerals.

When material acquiring positive charges at low pH values is present, the permanent charge of the clay mineral cannot be measured with certainty. In the case of the untreated Rothamsted subsoil clay, an estimate could be made by adding to the net negative charge found at pH 3 the change in the chloride adsorption between pH 3 and pH 7. This method of calculation can be justified in this case because there is a close correspondence between the rise in the net negative charge between pH 3 and pH 5 and the fall in chloride adsorption, showing that the negative charge remains practically constant over this pH range.

Between pH 6 and pH 7·5 there is a considerable rise in the negative charge of both the treated and untreated subsoil. This proves the existence of sites that are uncharged below pH 6, but can become negatively charged by loss of a proton to a water molecule at higher pH values. No doubt some of these sites are to be found along the edges of the silicon-oxygen sheets of the clay mineral. Here will be found some oxygens combined to only one silicon. These will exist as $-OH$ groups below pH 6 and be capable of dissociation to form $-O^-$ at higher pH values. We have, however, no assurance at present that these are the only sites where extra negative charges can develop, even when free ferric oxide has been removed.

The net negative charge carried by the untreated Rothamsted subsoil at pH 7·5 appears to be distinctly greater than that carried by the corresponding oxalate-treated material. No doubt a small amount of the clay mineral and, possibly, some free silica were lost in the course of the oxalate washing. The conclusion that the free ferric oxide can carry some negative charges is not a conclusion that can safely be drawn from these observations alone, although it is a possibility that should not be overlooked.

This investigation has failed to reveal the existence of sites that acquire negative charges by proton transfer in the range pH 4–pH 5. Bradfield's idea that clay is a weak acid of strength comparable with acetic acid appears to be wrong. Yet the Rothamsted clay can be freed of its exchangeable calcium, magnesium, potassium, and sodium by leaching with N/100 HCl. After the free HCl has been washed out, a

suspension of the clay when titrated with alkali gives a curve of the kind obtained by Bradfield, which shows that the greater part of the alkali that reacts below the neutral point is taken up between pH 4 and pH 5. In the opinion of the author these hydroxyl ions must have reacted with aluminium ions liberated during the acid washing, and been retained as exchangeable cations when the excess HCl had been washed away. The reaction of the acid clay with alkali is essentially the precipitation of aluminium hydroxide, not the dissociation of a weak 'clay acid'.

Less extensive measurements on a bentonite and a china clay indicate that the conclusions reached through this detailed examination of the behaviour of the Rothamsted subsoil clay will be found to be of general application.

The measurements reported in this paper were carried out under the author's supervision by Mr. John Rolfe.

Summary

A method is described for obtaining the net charge carried by a clay in equilibrium with an ammonium-chloride solution of known pH.

A measure is also obtained of the variation with pH of the chloride adsorption.

Results are reported for a sample of subsoil clay both untreated and also after repeated treatment with acid ammonium oxalate in sunlight.

A component consisting mainly of hydrous ferric oxide is dissolved away by the acid ammonium oxalate. It carries positive charges at pH 3, but not at pH 7.

The clay mineral in this subsoil is mainly of the illite type, and is not attacked by the acid ammonium oxalate. It carries a constant negative charge between pH 2·5 and pH 5, due presumably to isomorphous replacement. Additional negative charges develop with rise in pH above 6.

This subsoil does not contain a 'clay acid' comparable in strength to acetic acid. The buffering exhibited by the acid-washed clay below pH 6 is attributed to the precipitation as aluminium hydroxide of exchangeable aluminium ions.

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A CLIMATIC INDEX FOR THE LEACHING FACTOR IN SOIL FORMATION

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THE association of many of the major soil groups of the world with zones of climate and natural vegetation has naturally led to the study of the relationship between climatic conditions and the geographical distribution of soils. In view of the important part which is played by the degree of leaching in determining the character of the soil profile, climatic factors or indices which are correlated with the degree of soil leaching are obviously amongst those that may be sought, and the present contribution is restricted therefore to a discussion of the several indices which have been suggested in relation to this degree of leaching, both in terms of the geographical distribution of soils as exampled in Australia, and with respect to the drainage of water through soils and the use of water by native vegetation and crops.

The essential principle of all the methods that have been adopted for this purpose has been to correct for the decreasing efficiency with rising temperatures of the rainfall as a leaching agent or contributor to soil moisture.

Such approaches have been those of Lang [1], de Martonne and Aufrère [2], and Crowther [3].

It is recognized, however, that temperature in these cases has been used primarily as an index of evaporation, and many attempts have consequently been made to secure alternative indices of the evaporative power of the air, using either temperature alone or in combination with some function of the water-vapour pressure of the atmosphere that could be determined from the standard observations of temperature and relative humidity. These indices all derive from the Transeau ratio [4] of precipitation to evaporation from a free water surface. The Meyer ratio [5] of precipitation to atmospheric saturation deficit is one that has been more widely applied in view of the infrequency of direct observations on evaporation, it being assumed that saturation deficit is a useful measure of the evaporative power of the air. The Thornthwaite ratio [6] is an alternative method of securing an estimate of the Transeau ratio by means of rainfall and temperature alone. All such indices and ratios can naturally be used in determining the boundaries of climatic regions as defined by geographers, as was done by Köppen [7].

In the correlation between the geographical boundaries of soil groups and climatic factors the most useful ratio has proved to be that of Meyer, and in addition to the original work of Meyer for Europe, north Africa, and west Asia, Jenny [8] covered the United States, Prescott [9, 10] dealt with Australia, and Hosking [11] with India.

It has been obvious, however, for some time, with the increasing knowledge concerning the boundaries of soil zones and with more reliable information becoming available with respect to the measurement

of saturation deficit and evaporation, that the simple ratios P/E of Transeau or $P/s.d.$ of Meyer were not adequate in dealing with the widest range of climatic conditions.

The original ratio P/T of Lang has been subject to a re-examination by Volobuev [12] in the light of the most recent information concerning the world distribution of soil zones as compiled by Prasolov. Volobuev determined graphically the climatic boundaries of the major soil zones in terms of two rectangular co-ordinates: Precipitation and Temperature.

A similar presentation with respect to precipitation and saturation deficit in Australia was employed by Prescott [13] in dealing with Australian soils, but little advance was possible until more accurate boundaries of the soil zones were available.

Soil Boundaries in Australia in Relation to Rainfall and Saturation Deficit

For this correlation two publications are available, the author's *Soil Map of Australia* [14] and the *Meteorological Data* (1933) published by the Council for Scientific and Industrial Research in collaboration with the Commonwealth Meteorological Bureau. The values for saturation deficit were determined from the mean annual temperature based on maximum and minimum values and the mean annual relative humidity as determined daily at 9.00 a.m. local time for the 390 recording stations available in this publication.

These estimates of saturation deficit are not perfect, however, and are the subject of current investigation by the Meteorological Bureau.

Considerable areas of Australia are, moreover, subject to seasonal rainfall, so that leaching leading to podzolization may be active for part only of the year. Generally speaking, the inland boundary of the podzolized soils in South Australia and Victoria corresponds to a wet season of approximately 9 months' duration.

It should also be remembered that in Australia many soil zones bear the imprint of previous climatic cycles, the most important of which is the period of laterite formation in the Pliocene.

In the course of this experimental replotting of the two co-ordinates, annual rainfall and saturation deficit, it was found that the climatic boundaries between the several zones could not be expressed as straight lines through the origin as would have been the case had the lines been derived from the simple Meyer ratio of $P/s.d.$

The most efficient distribution was obtained when logarithms of both values were taken as co-ordinates. This is shown graphically in Fig. 1. The major soil zone for each recording locality is known in most cases and particular attention was directed to the climatic values for localities near well-defined soil boundaries.

Only five major soil groups were considered; podzols, red-brown earths, black earths, grey and brown soils, and desert formations. It was found that the black soils came within the same climatic grouping as the red-brown earths but, generally speaking, at the higher values of rainfall and saturation deficit.

The most characteristic climatic feature, as already mentioned, is, however, not shown in the annual values; the red-brown earths occur in

regions having characteristic seasonal rainfall and seasonal drought, whereas the black soils occur in the zone of transition from summer to winter effective seasonal rainfall.

The boundary between the red-brown earths and the podzols is that between Marbut's pedocals and pedalfers.

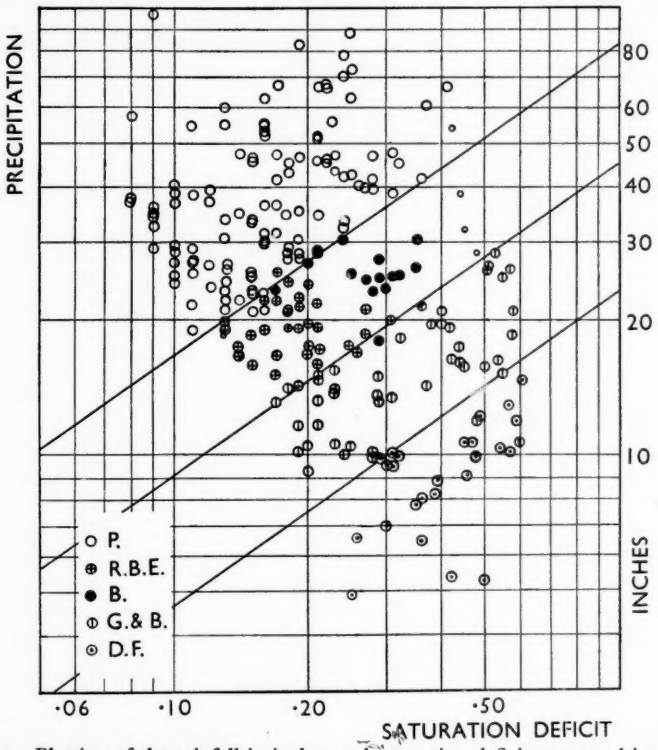

FIG. 1. Plotting of the rainfall in inches and saturation deficit expressed in inches of mercury of some 400 stations in Australia in relation to the dominant soil zone of the locality. A group of four stations in north Queensland where soil conditions are unknown is represented by small circles.

P., podzols; R.B.E., red-brown earths; B., black earths; G. & B., grey and brown soils; D.F., desert formations.

The lines dividing the points representing the several soil groups were found to be approximately parallel, and it proved convenient to bring them to the same slope of 0·70. The equation representing the boundaries between the several soil formations takes the form therefore:

$$\log P = 0{\cdot}7 \log s.d. + b,$$

or

$$\frac{P}{(s.d.)^{0{\cdot}7}} = K, \quad \text{where } b = \log K.$$

When P is expressed in inches of rainfall and *s.d.* in inches of mercury,

the values of K that can be regarded as the climatic indices for the several boundaries are given in Table 1.

TABLE 1

Values of the Climatic Index $K = \dfrac{P}{(s.d.)^{0.7}}$ *along the Boundaries separating Soil Groups in Australia*

Boundaries	*Climatic index*
Between desert formations and grey and brown soils	23
Between grey and brown soils and red-brown earths and black earths	45
Between red-brown earths and podzols	83

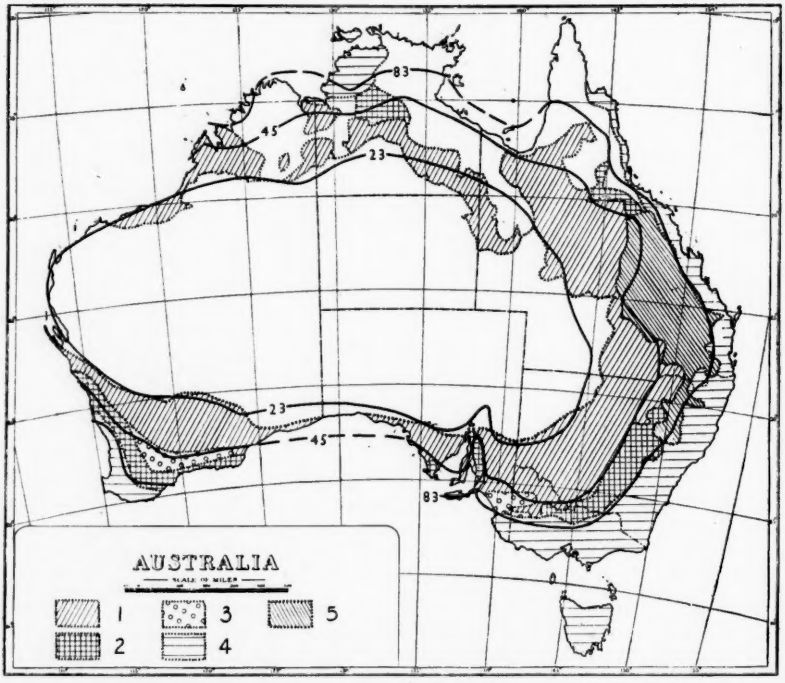

FIG. 2. Map of Australia with isologs of the climatic index $P/E^{0.7}$ projected against the boundaries of the major soil zones.

1, Grey and brown soils; 2, red-brown earths; 3, zones of marked solonization; 4, podzols; 5, black earths. The central area of desert formations is left unshaded. Blank areas in northern Australia are mostly occupied by tableland and range country with shallow soil formations.

Assuming that annual evaporation from a free water surface is equal to 258 *s.d.*, these values become 0·47, 0·92, and 1·70, respectively. In

Fig. 2 are illustrated on a map of Australia the boundaries of these major soil formations together with the isologs of the above climatic indices.

Evidence from the Records of Drain Gauges

The records of the Rothamsted drain gauges were examined by Crowther in his assessment of the leaching factor of soil formation in terms of rainfall and temperature.

The use of the percolation gauge for the study of evaporation from the soil was introduced in 1796 by Dalton in England and Maurice in Switzerland, and the relationship between rainfall, soil evaporation, and soil drainage was studied by means of such 'Dalton gauges' by a number of observers, until Lawes, Gilbert, and Warington [15] set up the famous Rothamsted drain gauges or lysimeters in 1870. The Rothamsted gauges differed from those previously used in that the blocks of soil concerned, each one-thousandth acre in area, were not disturbed during their construction. Two early English groups of observations were those near King's Langley by Dickinson recorded by Parkes [16] and Evans [17] and those at Lee Bridge conducted by Greaves [18]. The observations of Dickinson and Evans covered the period 1836 to 1875 and of Greaves the 14 years 1860 to 1873. Although it is presumed that the difference between rainfall and percolation represents evaporation from the soil surface, during short periods and for general monthly averages the fluctuations in the amount of water retained by the soil account for some of the differences. For annual periods, however, the deficiency may well be more equal to the actual evaporation from the soil surface.

Similar drain gauges were subsequently set up elsewhere, those probably best known being at Croydon, England [19], Craibstone, Scotland [20, 21], Pusa, India [22], and at Buitenzorg, Java [23].

The records for Lee Bridge, Croydon, Pusa, and Buitenzorg include measurements of evaporation from a free water surface.

The Rothamsted gauges have been kept under bare fallow, but many of the others have been systematically cropped or left under grass. The Rothamsted records have been the subject of systematic study and statistical examination, and reference will be made particularly to the work of Crowther [3] and of Sahni [24] in this connexion.

A statistical examination of these records shows that there is a close correlation between annual drainage and annual rainfall, but that the annual evaporation from a free water surface, where available, varies too little from year to year to allow the effect of evaporative power of the air on the drainage to be evaluated for any given gauge.

It may be assumed that for each site there is a value for the annual rainfall at which the statistical correlation indicates that the drainage would be zero, and this may be used as one basis for estimating the evaporation from the soil or ground cover. The rainfall corresponding to this nil drainage varies with the evaporation from 8·6 in. with an annual evaporation of 15·5 in. to 32·4 in. with an evaporation of 66 in. The results of the statistical evaluation of the data from these drain gauges are brought together in Table 2.

TABLE 2

Drainage through the Soil of Drain Gauges

Locality	*Length of record (years)*	*Fallow or crop*	*Mean annual rainfall P (in.)*	*Evaporation from free water surface E (in.)*	*Mean annual drainage D (in.)*	*Regression equations*	*Correlation coefficient*	*Calculated rainfall when D = 0 (in.)*
Based on annual values								
Lee Bridge, England .	22	Grass	25·7	20·6	7·5	$D = 0{\cdot}508P - 6{\cdot}2$	0·82	12·3
Croydon, England . .	30	Grass	25·5	18·1	10·6	$D = 0{\cdot}883P - 11{\cdot}9$	0·92	13·5
Rothamsted, England .	20	Bare fallow	29·6	18·1‡	15·3	$D = 0{\cdot}939P - 12{\cdot}4$	0·99	13·3
Craibstone, Scotland .	18	Crop rotation	34·7	15·5‡	18·4	$D = 0{\cdot}704P - 6{\cdot}1$	0·85	8·6
Pusa, India . . .	18	Bare fallow	47·6	53·5	14·6	$D = 0{\cdot}665P - 17{\cdot}0$	0·91	25·6
Pusa, India . . .	18	Sunn hemp*	47·6	53·5	12·7	$D = 0{\cdot}786P - 24{\cdot}6$	0·85	31·3
Buitenzorg, Java . .	..	Bare fallow	166†	66†	75†	$D = 0{\cdot}875P - 28{\cdot}3$	..	32·4
Based on 43 natural periods in summer months								
Rothamsted, England .	..	Bare fallow	45·9§	28·8§	15·7§	$D = 0{\cdot}543P - 9{\cdot}2$	0·91	16·9

* *Crotolaria juncea.* † One year only (1908). The regression equation is Mohr's own and is based on several years' observations.
‡ Estimated. § Calculated to annual rates from daily rates.

For these gauges the regression equation connecting rainfall at nil drainage with annual evaporation from a free water surface is

$$\log P = 0{\cdot}805 \log E + 0{\cdot}0577 \qquad (r = 0{\cdot}971)$$

or

$$\frac{P}{E^{0{\cdot}80}} = 1{\cdot}14.$$

The Rothamsted drain gauges

Crowther [3] examined the mean monthly values for 51 years of the Rothamsted drainage and obtained significant regression equations connecting monthly drainage with rainfall and temperature. These data have been re-examined in terms of estimated evaporation based on saturation deficit derived from relative humidity and temperature at Rothamsted, and the following series of regression equations obtained:

TABLE 3

Regression Equations connecting Drainage with Rainfall and Temperature or Evaporation at Rothamsted

	Regression equation	*Correlation coefficient*
1.	$D = 1{\cdot}920 + 1{\cdot}112P - 0{\cdot}0695T$	0·977
2.	$D = -0{\cdot}050 + 3{\cdot}841 \log P - 1{\cdot}807 \log E$	0·976
3.	$D = 0{\cdot}68 + 1{\cdot}89 \log P/E$	0·969
4.	$D = 0{\cdot}090 + 3{\cdot}47 \log P/E^{0{\cdot}54}$	0·989
5.	$D = -0{\cdot}578 + 0{\cdot}78P/E^{0{\cdot}40}$	0·992

Notes: 1. This is Crowther's original equation. 2. This equation corresponds to $P/E^{0{\cdot}47}$. 4 and 5. These equations correspond to the highest correlation coefficients.

All the regression coefficients are significant, and it is evident that a single-value climatic index of the form P/E^m is the one which is likely to be most efficient.

When leaching is nil the appropriate values of the above indices are shown in Table 4.

TABLE 4

Value of Climatic Index P/E^m for Different Values of m when Drainage is nil. Based on Mean Monthly Values of the Rothamsted Drain Gauges

	Value of m	*Value of P/E^m when $D = 0$*
	0·40	0·74
	0·47	1·03
	0·54	0·94
Mean	0·47	0·91

Use of Water by Crops and Native Vegetation

Of recent years information has become more generally available with respect to the amount of water used by crops and native vegetation under field conditions, and the information readily available in the literature

has been examined. Estimates have been made of the mean monthly losses by the combined transpiration and evaporation from the soil and of the evaporation from a free water surface during the corresponding period.

The data are recorded in Table 5.

TABLE 5

Water Losses in the Field from Vegetated Soils in Relation to Evaporation from a Free Water Surface

Locality	*Nature of ground cover*	*Transpiration and evaporation from plant and soil* E_s *(in. per month)*	*Mean probable evaporation from a free water surface* E_w *(in. per month)*	*Source of data*
Minsk, White Russia	Undrained bog*	2·38	1·65	Ivitsky [25]
	Drained bog	1·14	1·65	..
	Drained bog* with timothy	2·21	1·65	..
Rothamsted, England	Wheat in drought year*	3·07	2·74	Lawes and Gilbert [26]
Bahtim, Egypt	Irrigated maize*	5·31	4·92	Prescott [27]
Griffith, Australia	Irrigated lucerne	3·54	6·80	West [28]
Merbein, Australia	Irrigated vines	3·58	7·31	Research Station
Rehovoth, Palestine	Irrigated lucerne	4·22	7·70	Reiss [29]
Giza, Egypt	Irrigated cotton*	8·42	8·27	Balls [30]
Carlsbad, New Mexico	Sacaton,† water table at 2 ft.	6·08	9·85	Blaney and Morin [31
	Sacaton,† water table at 4 ft.	5·77	9·85	..
	Salt cedar,‡ water table at 2 ft.*	8·95	9·85	..

† Sacaton is *Sporobolus wrightii.* ‡ Salt cedar is *Tamarix gallica.*

The two quantities E_s and E_w in Table 5 are related by the regression equation

$$\log E_s = 0{\cdot}684 \log E_w + 0{\cdot}124 \qquad (r = 0{\cdot}857)$$

or

$$\frac{E_s}{E_w^{0{\cdot}68}} = 1{\cdot}33.$$

In the experimental plotting of these data it was noted that a group of six high values marked with an asterisk in Table 5 showed limiting values. The regression equation connecting the values of E_s and E_w for this group was found to be:

$$\log E_s = 0{\cdot}791 \log E_w + 0{\cdot}177 \qquad (r = 0{\cdot}997)$$

or

$$\frac{E_s}{E_w^{0{\cdot}79}} = 1{\cdot}50,$$

which may be taken to represent the relationship for freely transpiring vegetation well supplied with soil moisture. Where the rainfall balances the transpiration these values will correspond to the absence of drainage.

Transpiration in Relation to Evaporation

Further evidence with respect to losses of water from plants in relation to the evaporating power of the air may be obtained from an examination

of the records of experiments on direct transpirational losses such as were obtained by Briggs and Shantz [32, 33], Richardson and Trumble [34], and Maximov [35]. In the two former cases evaporation measurements were made at frequent intervals by weighing shallow pans adjacent to the pots containing the transpiring plants, and the records showing the most consistent relationship during the hours of daylight have been examined. These include the measurements made with lucerne at Akron, Colo., in October 1914 and July 1916 by Briggs and Shantz and with wheat and saltbush at the Waite Institute in November 1928 by Richardson and Trumble.

These experiments are not strictly comparable with either field conditions or with themselves owing to the different diameters of the pots and of the evaporating pans employed. The regression coefficients are, however, valid, being independent of these factors. They are recorded in Table 6.

TABLE 6

Transpiration (E_T) from Growing Plants in Relation to Evaporation (E) from a Free Water Surface during Daylight Hours

Regression coefficient in the equation $\log E_T = m \log E + b$

Locality	*Plant*	*Time interval*	*Number of sets of observations*	*Regression coefficient m*	*Correlation coefficient r*
Akron, Colo. . . .	Lucerne	hourly	10	0·803	0·964
Akron, Colo. . . .	Lucerne	2-hourly	18	0·581	0·967
Waite Institute, S. Australia .	Saltbush*	2-hourly	6	0·759	0·961
Waite Institute, S. Australia .	Wheat	2-hourly	6	0·670	0·996

* *Atriplex semibaccatum.*

The results for the South Australian examples are shown graphically in Fig. 3.

Conclusions

The conclusion to be drawn from a number of independent lines of evidence therefore is that the climatic index which can most efficiently represent the relationship between the use of water by vegetation and the evaporation from a free water surface is of the type

$$P/E^m,$$

where P is the rainfall and E is the corresponding evaporation from a free water surface.

The drainage through the soil is related to this index by the regression equation

$$D = \log \frac{P}{E^m} + k,$$

and the index is likely to have a specific value for the determination of the geographical boundaries of soil groups and the use of water by vegetation

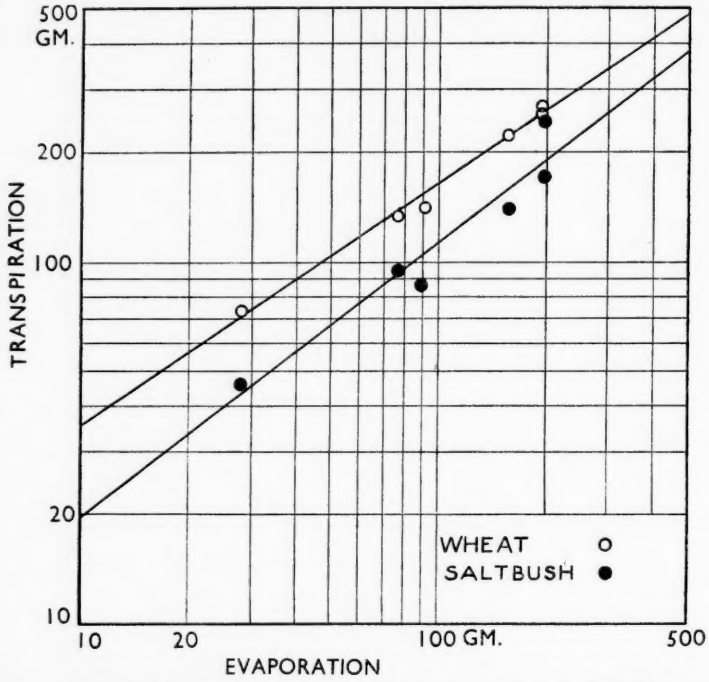

FIG. 3. Relationship between transpiration and evaporation in daylight hours at the Waite Institute in the experiment of Richardson and Trumble. The equations of the regression lines illustrated are:

$$\text{for wheat: } \log E_T = 0{\cdot}67 \log E + 0{\cdot}87$$
$$\text{for saltbush: } \log E_T = 0{\cdot}76 \log E + 0{\cdot}53.$$

and crops. The value of m in the index varies from 0·67 to 0·80 as indicated in the summary Table 7, with a mean value of 0·73.

TABLE 7

Values of m and of the Climatic Index P/E^m

	m	P/E^m	
Geographical boundaries of soil groups in Australia	0·70	0·5 1·7	for desert margins. for the separation of pedocals and pedalfers.
Records of drain gauges (annual and natural periods)	0·80	1·1	for nil drainage.
Use of water by field vegetation:			
for all examples	0·68	1·3	when rainfall balances transpiration.
for freely transpiring vegetation	0·79	1·5	
Transpiration measurements:			
Lucerne	0·69	..	..
Wheat	0·67	..	..
Saltbush	0·76	..	..

Summary

Evidence has been obtained from the examination of soil boundaries in Australia, the records of drain gauges, the use of water by field vegetation, and the measurements of transpiration that the most efficient single-value climatic index is P/E^m where P represents precipitation, E evaporation from a free water surface, and m is a constant varying from 0·67 to 0·80 with a probable mean of 0·73. A value for this index of 1·1 to 1·5 corresponds to the point where rainfall balances transpiration from vegetation and evaporation from the soil.

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FROST SOILS ON MOUNT KENYA, AND THE RELATION OF FROST SOILS TO AEOLIAN DEPOSITS

F. E. ZEUNER

WITH PLATES I AND II

IT is well known that frost causes movements of particles in the soil. Every gardener makes use of the fact that frost breaks up the clods of earth when he digs his plot in autumn and leaves the rough ground exposed through the winter. Observers of the soil will have noticed that pebbles and stones are sometimes raised above the ground-surface on pillars of ice after a night frost, as a rule following a thorough previous wetting of the ground by rain. It is less generally known, however, that in certain types of frost climates, mainly in arctic, sub-arctic, and mountainous regions, frost produces highly peculiar structures in the soil, extending down to a depth of several feet, and with geometrical patterns of sorted material on the surface. These structured frost soils have been the subject of many investigations by geologists and geographers interested in climatic phenomena. As a present-day phenomenon, they are of considerable importance in cold climates, where weathering of the bed-rock is almost entirely the result of frost action. On a much smaller scale these processes play their part in temperate regions with winter frosts [for Britain see 1, 2, 3], and even here they are liable to cause damage to buildings and roads. They are, therefore, not merely of academic interest, and in cold climates are of great practical importance [4]. To the geologist their prime interest lies in the occurrence of fossil frost soils in Pleistocene deposits, where they prove the prevalence of certain climatic conditions at certain times in the past [5]. In recent years American workers have felt the need of putting the nomenclature of frost soils on a firmer footing [6], and a term has even been suggested for the study of frost action in soils, viz. cryopedology.

In the present paper it is not intended to give a survey of the numerous frost phenomena that have been observed, since a number of good accounts are available [4, 7–14], but to draw attention to the presence of a particular type of soil structures in the high mountains of the equatorial zone of Africa, where they appear to be formed by diurnal, not seasonal, fluctuations of temperature and therefore are more easily studied than in the cold regions of high latitudes and mountains of the temperate zone. The structures in question are miniature stone nets and stone stripes, observed on Mount Kenya at an altitude of 13,000–14,000 ft. (Pl. I, Fig. 1). At this altitude the climate appears to be characterized by a lack of clearly defined seasons. There are frequent rainstorms and snowfalls, but, the mountain being crossed by the equator, sunshine heats the ground sufficiently to prevent the formation of snow-fields. When the sky is clear, the ground is heated considerably in daytime, but during the night heavy radiation frosts occur. During the night of 8 February 1947, when I camped with Mr. Raymond Hook above the Mackinder Valley, where the frost soils are very conspicuous, prismatic

ice-crystals ('needle ice') 2½ in. long formed in superficially dry stream beds, and the ground froze to a depth of about 2 in. But during the day, heating by the sun removed the frost completely.

The subsoil on which the frost soils were most in evidence was a 'gravel', more precisely, angular debris of porphyritic Kenyte lava, with large phenocrysts of anorthoclase feldspar in a fine matrix [15]. This 'gravel', which was normally composed of fragments of 2 in. diameter and less, occurs in the shape of talus slopes (Pl. I, Fig. 2) which flatten out in places. On strongly inclined surfaces striped soil structures are observed (Pl. II, Fig. 3), whilst the less steeply inclined and more or less level surfaces bear structures of the network type (Pl. II, Fig. 4). The structures are by no means found everywhere. They were most frequent in a cirque-shaped hollow (Campi Sheitani) at an altitude of about 13,000 ft. That the soil stripes are causally connected with the soil nets is evident from numerous transitional structures, as shown in Pl. II, Fig. 5. Though this must not be interpreted as meaning that all types of striped soils are the slope variants of net soils, it may be assumed that in this instance (as in many others) any explanation put forward for the stone nets will, *mutatis mutandis*, apply to some of the stone stripes also, and these are therefore left out of the present discussion.

The stone nets on Mount Kenya differ from those found in the north by their small size. The fine-earth centres are only 5–8 in. in diameter, and the width of the stony borders which separate them varies from 1 to 4 in. (Pl. II, Fig. 4). The centres are raised above the borders and form a hard cake which can be lifted off easily, even when not frozen. They are about 1 or 2 in. thick and consist mainly of dusty material (for mechanical analysis see below) mixed with small grit, but containing very few coarser stones. A curious feature is the presence in them of round holes one to several millimetres in diameter that give them a vesicular texture, superficially almost reminiscent of the vesicular lava found in the neighbourhood. It is improbable that these vesicles are due to the freezing process which is dominated by the formation of needle ice. The only explanation that I have been able to think of so far is that intense diurnal heating of the wet mud cakes causes evaporation as well as expansion of any air enclosed, so that air and steam bubbles are formed. This is admittedly a suggestion which I venture to make solely for want of a better one. It must not be overlooked, however, that at high altitudes under the equator the diurnal changes in temperature and humidity of the soil are enormous. Soil which is solidly frozen at night thaws every day, and under the influence of the sun soon becomes hot to the touch. Under 48° N. latitude soil temperatures as high as 68° C. have been measured [16]. It is conceivable, therefore, that in the equatorial zone even more intense heating might occur.

The borders, consisting of coarse fragments of the order of ¼–1 in. diameter, are free from fine-earth. They extend to a depth of about 1 or 2 in., i.e. to about the same depth as the fine-earth centres. Beneath both centres and borders unsorted material is found, an unstratified mixture of fine-earth with the coarse fragments. It is of a loose texture, not caked as are the centres, and it was wet when studied. This wetness of the

unsorted subsoil appears to be a prerequisite for the development of soil structures on Mount Kenya, since in places where the drainage was good, as in certain large talus slopes (Pl. II, Fig. 6), the soil structures were generally absent.

In daytime the stone nets just described were fairly dry when I saw them. But as there had not been a heavy fall of snow or rain, it is not to be implied that this is their usual condition. Most probably the fine-earth centres will absorb large quantities of water when it rains or when snow melts and thus become sufficiently plastic for sorting processes to occur in them. It thus appears that the soil structures are dormant while dry, and that sorting occurs only when the surface soil has been wetted, as happens quite frequently on Mount Kenya.

During the night intense frosts occur. We had no thermometers, but Pl. II, Fig. 6, illustrates that very low temperatures are reached. This figure shows a talus slope which is built up of dry and loose material (note footprints on the right). From a gap in the cliff in the middle of the background a stream of water had rushed down this slope, which at the time seems to have had a temperature much below freezing-point. The water which would have seeped into the loose gravel froze on contact, and built up a stream bed with levees consisting of its own frozen load, over a distance of the order of 100 ft., before it was all used up in the process of filling the gravel with ice and thus forming a bed for itself.

Other superficially dry stream beds in the 'cirque' at Campi Sheitani produced needle ice $2\frac{1}{2}$ in. high in the course of the night, each bunch of needle ice carrying as a cap a feldspar crystal or some other fragment of rock. The ice disappeared in the daytime, but its presence showed that capillary ice growth, drawing on the store of water below the dried-up surface, and with the lifting of coarse particles, is an ordinary occurrence in this area.

The miniature stone nets of Mount Kenya differ from related structure soils in arctic regions not only in size. The other characteristic is the absence of tjaele (permanently frozen subsoil). It appears that in mountainous regions in the temperate zone the place of the tjaele may be taken by an impermeable rock-surface [5]. As regards the mode of formation, therefore, of the stone nets of Mount Kenya which rest on loose talus, theories requiring an impermeable floor, either of rock or of tjaele, can be ruled out. Valuable evidence is here provided that the presence of an impermeable floor, which many workers regard as one of the conditions for the formation of structure soils [13, p. 113], is in fact not essential. On the other hand, the conspicuous presence of needle ice makes one inclined to consider this agent as significant. In other words, 'frost-heave' and 'frost-shove' produced by needle-ice formation appear to be the main cause of the sorting in the Mount Kenya type of frost soil, and possibly the sole cause.* When in the dry condition, the caked centres of the stone nets were found to be slightly lifted up by ice in the morning. This of course merely shows that frost-heave occurs in these stone nets; for the sorting of the material and transport of the stones

* The importance of needle-ice heave has been stressed by Taber [17, 18], Hamberg [19], Hay [2], and others.

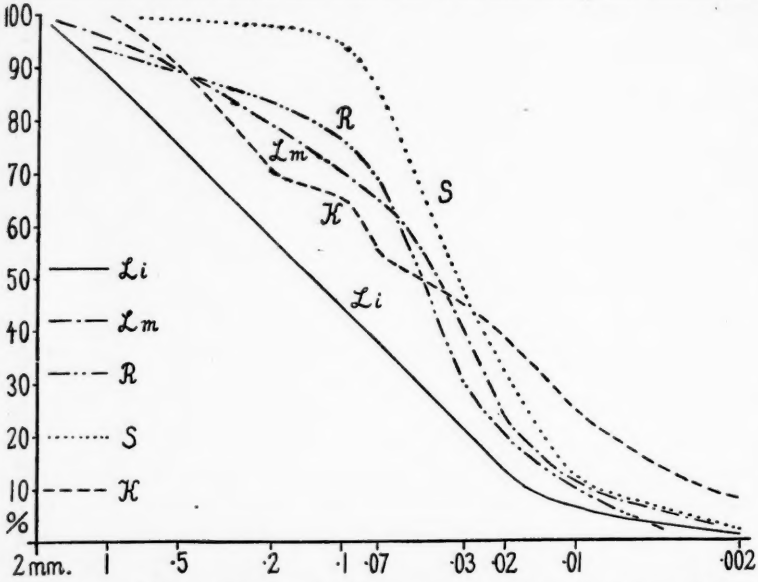
towards the periphery the material must be sufficiently wet to allow the particles to separate. Though the observations made on these frost soils of Mount Kenya are of a casual character, they appear to show that a type of structure soil is found here which (*a*) depends on daily instead of seasonal freezing, and (*b*) does not require an impermeable floor.

When studying these structures I noticed that in the sorted stratum the amount of 'fine-earth' relative to the amount of stones concentrated in the nets is greater than the amount of fine-earth contained in the unsorted substratum. This suggested that sorting is not the only process which occurs in these frost soils, and that the amount of fine-earth is actually increased, probably by frost-splitting. Most students of frost soils have concentrated their attention on the processes of sorting. Following Nansen [20], however, Beskow [4] and Dücker [21] have pointed out that the concentration of fine sand and silt observed in many frost soils is not merely the result of sorting but also of an actual increase due to frost-weathering. Frost-weathering depends on the breaking up of stone into smaller fragments by freezing pressure, exerted by water contained in fissures and cracks. It is a well-known phenomenon on the macroscopic scale. Since all frost soils contain few or no particles of the clay grade, there appears to be a limit to the breaking down by frost action at about 0·01 or 0·002 mm. diameter. Beskow [8, p. 632] holds that this limit is due to the lowering of the freezing-point in very fine cracks. An alternative explanation is that particles of this size are sufficiently elastic to respond to freezing-pressure without fracturing [5, p. 5]. Whatever the cause, the existence of such limit should lead to the concentration of fragments in the grades just above it. Fully mature frost soils, therefore, should contain a high percentage of silt.

Mechanical analysis provides a means of testing this. In Text-fig. 1 are shown a number of analyses of fine-earth from various types of frost soils. Beskow [8] noticed that the grading of immature frost soils differs from that of mature ones in the presence of a large amount of coarser material. As an example, one of his immature frost-soils from Norra Storfjället, Lapland, is shown in Text-fig. 1 (*Li*). There is no concentration in the grades above 0·01 mm. and all grades contribute almost exactly equal portions to the soil above 0·02 mm. Smaller particles are present in very small quantities only. On the other hand, concentration is noticeable in one of the mature frost soils from the same locality (Text-fig. 1, *Lm*), and even more so in a specimen from a stone ring in the Sudeten Mountains (Text-fig. 1, *R*) studied by Dücker [21]. It is most conspicuous in a striped soil from Spitsbergen (Text-fig. 1, *S*), with 82 per cent. between 0·01 and 0·1 mm. All these soils have in common the scarcity of material in the finest grades, especially below 0·002 mm. This suggests that there is indeed a limit of grain size below which little or no frost-splitting occurs, and that this limit lies near 0·01 mm.

If one examines fine-earth from one of the centres of the frost soil from Mount Kenya, one finds that this material is intermediate between the immature and the mature types of fine-earths. But in addition it exhibits several peculiarities. The most striking is the irregular course of the summation curve. It exhibits three 'bulges', of which that at

0·1 mm. is particularly pronounced, suggesting that this grain size is somehow favoured by disintegration and receives a relatively larger accretion than those above and below it. The microscopical examination



TEXT-FIG. 1. Mechanical analyses of fine-earths from various frost soils. *Li*: from solifluxion layer, Norra Storfjället, south Lapland, Sweden; example of an immature frost soil. *Lm*: from striped soil, Norra Storfjället, south Lapland, Sweden; a mature frost soil. *R*: from stone ring on Riesengebirge, Sudeten Mountains, 4,800 ft. above sea-level, a mature type. *S*: from striped soil, Spitsbergen, a mature type. *K*: from stone net, Mount Kenya, 13,000 ft. above sea-level, an immature type.
Analyses: *Li*, *Lm*, [8]; *R*, [21]; *S*, *K*, by the author.

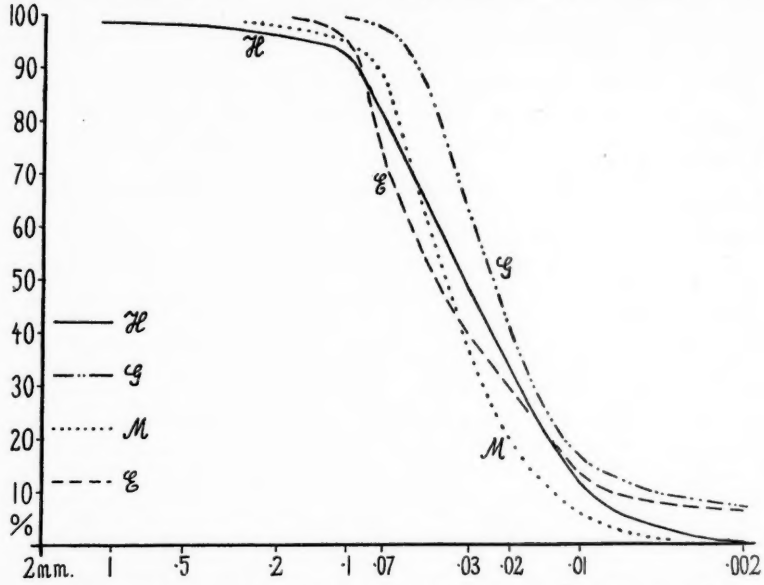
confirmed that this anomaly is caused by the anorthoclase feldspar, which is present in the following proportions:

Grade	*Anorthoclase*	*Other constituents*
1–0·5 mm.	7	10
0·5–0·2 mm.	5·8	10
0·2–0·1 mm.	4·2	10
0·1–0·07 mm.	5·1	10
0·07–0·03 mm.	2·6	10

This table shows that, on the whole, the number of anorthoclase phenocrysts decreases with decreasing grain size, except in grade 0·1–0·07 mm., where there is an increase. If one assumes that anorthoclase was decreasing normally, and calculates the amount of material to be expected in grade 0·1–0·07 mm. in this case, one finds that the bulge in the summation curve disappears.

The cause of the anomalous behaviour of the anorthoclase is conceivably its cleavage, which might lend itself to the production of

fragments of this particular size. Alternatively, the original rock might primarily contain a large number of phenocrysts of this size.* Abnormalities in the grading of coarser deposits have been known for some time, and it was found that they are either due to the existence of an optimum cleavage in the contributing rocks or the release by disintegration of certain crystals. As an example for the first alternative the



TEXT-FIG. 2. Mechanical analyses of true, unweathered loesses. *H*: Hárshegy, Budapest, Hungary. *G*: Gaza Pit, Gnadenfeld, Upper Silesia. *M*: Carrière Chemin-de-fer, Montières near Amiens, France. *E*: 'Upper middle loam', Ebbsfleet near Gravesend, Kent.

Analyses by the author.

increase of feldspar in certain river gravels in the grade 5–3 mm. may be mentioned, the material being derived from syenites and gneisses. As to the second alternative, quartz porphyry is known to yield quartz crystals in the grade 3–2 mm. in quantities which affect the result of the analyses [22].

The second peculiarity of the frost soil from Mount Kenya is the presence of a fair amount of material in the grades below 0·01 mm. For this I am unable to suggest an explanation.

It has been pointed out above that in fine-earth from mature frost soils the silt grades, between 0·1 and 0·01 mm., tend to predominate. This fact is most interesting from the point of view of loess distribution. Following Richthofen's observations on loess in China [23, p. 74], the theory that loess is wind-transported dust has become widely accepted,

* Dr. Campbell Smith informs me that he considers the first alternative the more probable.

and it has been applied to the vast deposits of Pleistocene loess in Europe, which extend from southern England to the Caspian Sea.

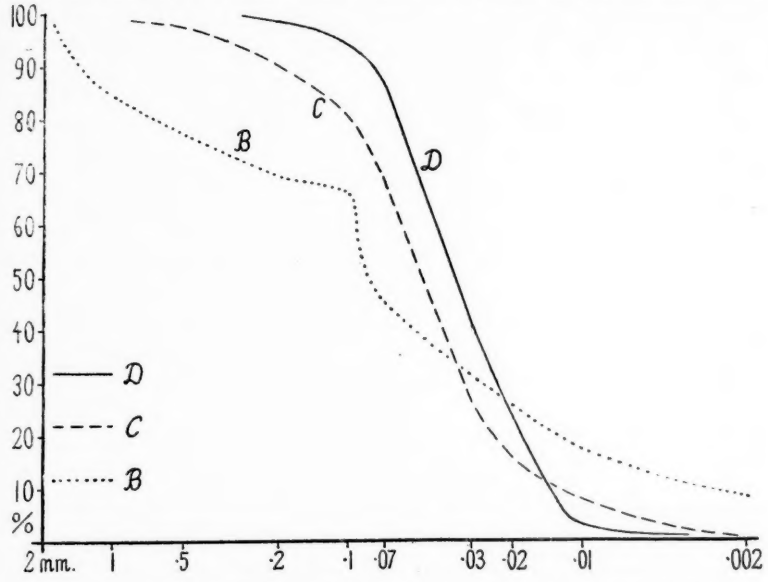
Now, loess exhibits the same predominance of the silt grade which we have observed in mature frost soils [5, 21]. Four examples are shown in Text-fig. 2, of loess from Hungary, Silesia, France, and England. They resemble strikingly the mature frost soil from Spitsbergen, Text-fig. 1, *S*. It has been suggested that such resemblance is not accidental but that frost-weathering provided the vast amount of dust deposited in the loess belt of Europe. If this is right, the puzzle of the provenance of the European loess would be solved, since it has always been one of the difficulties of the aeolian theory that bare gravel surfaces, moraines, hill-sides, &c., would not have been able to supply all the material deposited as loess.

One might even be inclined to discard aeolian transport and to assume that loess is a soil formation resulting from physical weathering *in situ*. This view would not be identical with that of the Russian geologist Leo Berg [24], who holds that loess is formed *in situ* by chemical weathering and coagulation of particles of the clay grade by calcium carbonate. Both views, however, would require formation *in situ* without transport of the particles, and geological opinion is almost unanimously agreed that loess is a genuine sediment. It appears to me that the most conclusive evidence against formation of loess *in situ* is the large number of sections containing several horizons of loess separated by fossil soils of the podzol, brown-earth, or chernozem type. It is impossible for a new layer of fresh loess to form by any suggested weathering process on top of an ordinary weathering soil developed on some older loess, without obliterating the soil profile.

If, then, it is necessary to assume transport, the agent suggested by mechanical analysis is wind. In Text-fig. 3 a few undoubtedly wind-borne dusts are shown. The most instructive is the recent dust from Breslau, Silesia (Text-fig. 3, *D*), which was collected after a strong wind had carried dust from the town and deposited it on snow. It contained a large amount of particles of typically urban origin (slag, brickdust, plant-fibre, soot, &c.). This dust shows unmistakably the grading of a 'loess'. Similarly, the cryoconite from Spitsbergen is a wind-borne dust deposited on the surface of a glacier. Again its grading is of the loess type, but, of course, also of the type of mature frost soils from which the material may well be derived.

It appears, therefore, that physical weathering, as demonstrated in the present paper for frost-weathering, produces a dust of a grain size which happens to be eminently suitable for transport by air currents. If one raises the question why this range from 0·1 to 0·01 mm. should be so favoured, it is not difficult to explain the upper size limit. According to Kölbl [25], the rate of sedimentation from air rises with increasing size of the particles so rapidly that grains of more than 0·06 mm. diameter are unlikely to be carried far in suspension by air currents. Their rate of sedimentation is 50 cm./sec. Above this size the sedimentation rate increases very rapidly, being 167 cm. for particles of 0·1 mm. diameter, and 250 cm. for those of 0·2 mm. Udden [26] calculated the distance

over which particles of different sizes are liable to be carried by wind. He found that grains of 0·06–0·03 mm. would still be carried some 200 miles, but grains of 0·13–0·06 mm. only a 'few miles'. Above this size no more than local shifting is normally achieved by the wind. A rapid decrease in the effectiveness of wind transport occurs between 0·06 and roughly 0·1 mm. This is indeed reproduced by the summation



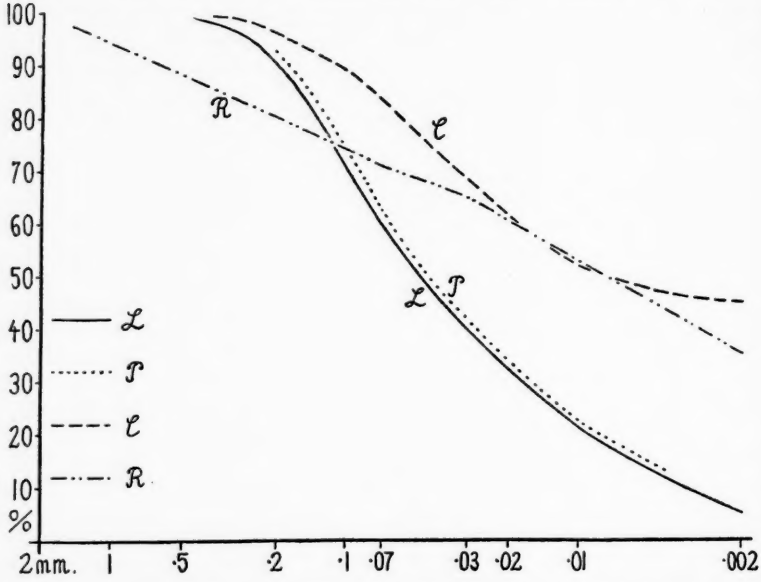
TEXT-FIG. 3. Mechanical analyses of wind-blown dusts. *D*: Dust collected on snow, east of the city of Breslau, Silesia, after a spell of west winds carrying dust from the city. *C*: Cryoconite, from Green Bay Glacier, Spitsbergen. *B*: Volcanic ash from northern Tanganyika, probably from Lemagrut volcano in the Ngorongoro chain, deposited on the edge of the Balbal depression. Wind is constantly playing with this material, and numerous dust-devils are seen. The curve suggests that wind-sorting is only beginning and, since the material has not been transported far, a fair amount of particles larger than 0·1 mm. is present.
Analyses by the author.

curves for loesses, Text-fig. 2. Bagnold [27, p. 6] approached the problem from the other side, that of the sand. According to this author the tendency of the particles to be carried up into the air and to be scattered as dust increases rapidly below 0·2 mm. In the finest wind-blown sands the predominant diameter is never less than 0·08 mm. These figures again suggest that the limit between wind-blown sand and dust lies, very approximately, near 0·1 mm., which value also is the mean of those accepted by Kölbl (0·06 mm.) and Bagnold (0·2 mm.), respectively.

The lower limit observed in wind-blown dust near 0·01 mm.* appears

* Since the analyses are intended to reveal the grading of the deposits as they occur in nature, all were carried out on samples prepared by shaking only. No dispersing agents were applied in order to avoid changes in the natural grading of the material.

to be determined by the co-operation of two factors. The first is the sedimentation rate which, according to Kölbl [25], is very slow for particles of less than 0·02 mm. diameter. It is conceivable, therefore, that dust particles much below this size remain suspended in air almost indefinitely, and that they are scarce in loesses for this reason. On the other hand, a varying proportion of 'clay-grade' particles *is* found in



TEXT-FIG. 4. Mechanical analyses of floodloams and other deposits superficially resembling loess. *L*: Floodloam of the Thames, Lavender's Pit, Shepperton, Middlesex. *P*: Floodloam of a small river at Psychod, Upper Silesia. (Both *L* and *P* may contain particles derived from loessic deposits.) *C*: Floodloam of the Neckar at Cannstatt near Stuttgart, west Germany. *R*: 'Terra Bruna' of Grotta Romanelli, Apulia, south Italy, probably blown into the cave by wind, but derived from soils of the Terra Rossa type found in the neighbourhood, and mixed with blown sand.
Analyses: *C*, Laufer and Hötzel in Soergel [29]; *L*, *P*, *R* by the author.

loesses, especially in weathered loesses from which the calcium carbonate has disappeared. Grahmann [28] emphasizes that certain Chinese loesses contain up to 40 per cent. of particles below 0·01 mm., but it may be assumed that the samples were dispersed with hydrochloric acid prior to analysis. Unweathered loesses which have not been dispersed artificially rarely contain more than 20 per cent. of the grades below 0·01 mm., and usually much less. In practice this affords a means of distinguishing certain types of flood loams from loesses (Text-fig. 4, *C*).

The second factor which tends to reduce the amount of particles below 0·01 mm. appears to be coagulation by calcium carbonate. Very few unweathered loesses are known which do not contain at least a few per cent. of calcium carbonate, and Berg [24] has pointed out (though in

order thus to explain the origin of the loess altogether) that the presence of calcium carbonate increases the amount of particles above 0·01 mm. at the expense of the clay. The two factors in combination, therefore—namely, permanent suspension of the finest particles in the air, and coagulation of such particles by calcium carbonate—appear to explain the lower limit of the 'loess grade' in a satisfactory manner.

Thus one arrives at the conclusion that the identity in grading of fine-earths from mature frost soils and of wind-borne dust deposits like loess is a coincidence. This coincidence explains why there are enormous dust deposits, i.e. loess, in a belt bordering the formerly glaciated areas of the northern hemisphere. Here frost-weathering prepared enormous quantities of material which could readily be carried away by the wind.

In the border zones of hot deserts, dust deposits are rare, and one is inclined to interpret this as due to the absence of frost-weathering. But dust is by no means absent, and the question whether insolation weathering (heat-fracturing) produces similar grades as does frost-weathering remains to be investigated.

Summary

1. Structure soils due to frost action occur on Mount Kenya at about 13,000–14,000 ft. altitude.

2. The stone nets of Mount Kenya belong to the group of frost soils formed by the action of needle ice.

3. The grading of the fine-earth shows that the Mount Kenya structures are immature, and that the disintegration of the crystals of anorthoclase produces certain irregularities in the grading.

4. Fine-earth from mature frost soils is predominantly composed of the silt-grade, from about 0·01 to 0·1 mm.

5. Wind-borne dust has the same grading, but from different causes.

6. The coincidence of 4 and 5 explains the wide distribution of loess in the periglacial areas of the northern hemisphere.

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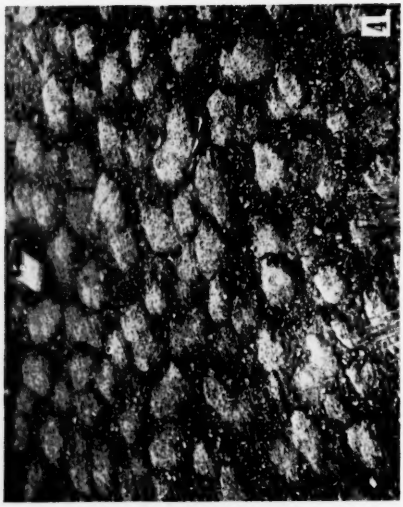
FIG. 1. General view of Campi Sheitani, the area of frost soils above the Mackinder Valley, 13,000–14,000 feet, with summits of Mount Kenya in the distance

FIG. 2. Talus slope above Campi Sheitani, composed of fragments of lava produced by frost splitting, and vegetation, mainly of giant *Senecio*, encroaching on it. 13,500 feet

PLATE I



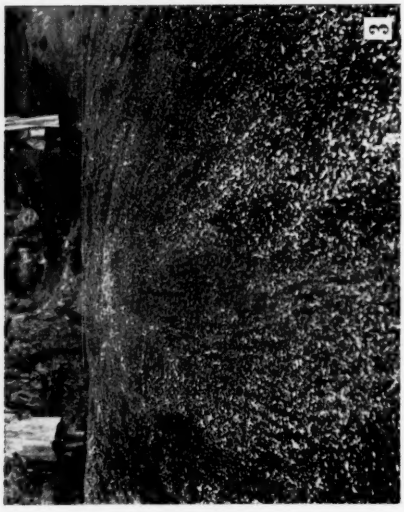


FIG. 3. Striped soil on talus slope, site near that shown in Fig. 2
FIG. 4. Stone-nets at Campi Sheitani
FIG. 5. Stone-nets passing into striped soils at Campi Sheitani
FIG. 6. Ephemeral stream, frozen on dry talus, above Campi Sheitani. 13,500 feet

PLATE II

GEOMORPHOLOGY AND SOIL SCIENCE

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EVERYONE familiar with the study of the soil in the field is aware of the importance of what is rather vaguely called topography. Under English conditions it is perhaps only second to parent material as the determinant of soil series or type. Even the so-called micro-relief is a powerful differentiating factor, and in the concept of a soil catena as developed by Milne the dominance of surface morphology is clearly to be seen. The direct effects of surface morphology on soil type are often, indeed, so obvious and, in a sense, simple that it might seem that little more is necessary for studying this aspect than a closely contoured map supplemented by eye inspection on the ground. One does not need to be a geomorphologist to recognize the distinction between convex and concave slopes and innumerable other minutiae of the land surface relevant to the task in hand.

It is perhaps less clearly realized that geomorphology has more to offer to the student of soils than the description and mapping, however accurate, of surface features. Its aim is to study the evolution of the landscape, and its essential subject matter is the *surfaces* of the land. There is, indeed, a veritable geology or geography of surfaces as distinct from rocks or strata, and it is on the geomorphological surfaces that soils form. In so far as the history of these surfaces is decipherable the contribution of geological science to pedology is far from limited to the mere provision of a schedule of parent materials. To speak of the history of such surfaces implies that they have a definite geological age, and it is the fact that surfaces differ in age and therefore in duration of exposure to pedogenic processes that has been unduly neglected in soil classification. One can, indeed, think and speak of the 'age of the site' in a much wider and more fundamental sense than that commonly used.

The Chalk areas of southern England afford a good example of surfaces or facets of different ages. At first sight the geology of these areas appears deceptively simple. Over the higher Chalk tracts the drift map supplements the solid-geology map only to the extent of showing an undifferentiated mass of 'plateau drift', comprising the Clay-with-Flints, plateau brick-earth, and various assortments of colluvial rock-rubbish. Yet there are notable variations in soil character, and before we ascribe them entirely to non-geological pedogenic factors we must certainly pause and note the complex form and history of the Chalk dip-slopes.

Taking, first, the Chilterns as an example, the highest ground between 650 ft. and the scarp crest is part of what has been termed the Mid-tertiary peneplain produced by long-continued erosion of the land area raised by the Alpine earth-movements. At the time of the original folding these areas carried a cover of Eocene rocks, but during the succeeding long period of erosion, roughly equivalent to the Miocene period, this cover was stripped and erosion bit deep into the underlying Chalk,

reducing it to a wide-spreading, undulating plain of which restricted remnants now survive only on and around the highest escarpment summits.

Over parts of the peneplain a Pliocene sea later advanced; its waves cut a bench in the Chalk at a remarkably consistent level of 500–650 ft., and this bench is separated from the unsubmerged land near the scarp crest by a distinct bluff which marks the position of the Pliocene coast-line. On the bench and beyond its present limits where the sea-floor passed on to Eocene rocks, a thin veneer of sand and shingle was spread; of this only scant remnants now survive.

Over lower portions of the Chalk dip-slope, below 500 ft. and adjoining the main Eocene outcrop, the general surface slope is steeper than on the Pliocene bench. We are dealing here essentially with the sub-Eocene surface or a close approximation to it, from which the Eocene cover and any succeeding Pliocene deposits have been stripped.

Here then are the three distinct facets of the Chiltern dip-slope. The same facets are even better developed throughout the North Downs dip-slope. They are traceable with more difficulty in the South Downs, where general dissection is more advanced, and recur at intervals throughout the extensive Chalk terrains of Hampshire, Berkshire, Wiltshire, and Dorset [1].

It is at once apparent that we are entitled to expect some differences in soil character reflecting the different physiographic history of these three facets. The first and highest has been continuously exposed to the atmosphere since some phase of Miocene times—certainly for a major fraction of 30 million years. The Pliocene facet was thinly covered with sand and shingle when the sea-floor was first uplifted, and distributed shreds and patches of this material survive to contribute to soil parentage, but the duration of exposure of such remnants and of the underlying Chalk must have been substantially less than half that of the 'Miocene facet'. The greater part of the third or sub-Eocene facet was not exposed to atmospheric attack until much later times, when the Eocene cover was breached and stripped back. It is clear that these facts carry the implication of a 'maturity sequence' in the soils such as was claimed by Saint in Barbados [2]. Here, on a uniform parent of coral limestone, the soils grade from red at elevations above 700 ft. through intermediate stages to black below 200 ft. and the facts were interpreted as marking stages of uplift of the island, and varying exposure to weathering of the successive emergent zones.

One turns to inquire what actual evidence there is of differences in soil or subsoil between the three Chalk facets. There is no complete soil survey which covers all three elements, but it must immediately appear as significant that true Clay-with-Flints, the simple solution residue of the Chalk, is largely confined to the Miocene facet. I have yet to see an indisputable exposure of such on the Pliocene facet, and it is conspicuously absent from the stripped sub-Eocene surface. Locally also a marked difference in land utilization is apparent between the three areas. Thus, the true plateau beechwoods of the Chilterns are largely confined to the Miocene facet, where they are associated with much true heath. In east

Kent the contrast in land-use pattern between the sub-Eocene and Pliocene surfaces is striking, the former with wide-spreading, hedgeless arable fields and the latter with poor grassland and coppice giving what to a Frenchman would be a typically 'bocage' landscape. These facts are sufficient to encourage the hope that the postulated differences are not entirely illusory. A direct attack on the problem will present certain difficulties. The prevalence of cultivated soils with imperfectly known short-period histories, in human and vegetational terms, confuses the issue, as also does the fact that all three facets and their soils bear the stamp of a million years of fluctuating Pleistocene climates and have suffered not only reconstruction but direct accession during this period. It might well be, indeed, that the vagaries of the short-term history, physical and human, have overpowered and masked the features of any major maturity sequence. Yet it must be noted that the expected variation would reflect not only major differences in the length of exposure to pedogenic processes but also real contrasts in the parent regolith above the Chalk. It may perhaps be mentioned that the valuable work of A. S. Watt on the Chiltern beechwoods [3] was largely confined to the highest or Miocene facet; it would be highly interesting to bring the pedological and ecological details of selected tracts of beechwood on the other facets into comparison with the facts he has recorded.

Whatever conclusions are ultimately reached on the particular case I have instanced, it is necessary to emphasize that the type of relationship sketched is a perfectly general one and the principles involved require general attention. English methods of soil survey rightly and inevitably accord high importance to the 'parent-material' factor, but wide areas are underlain by thick geological formations not amenable to fine lithological subdivision. It is particularly in such areas that morphological considerations assume a dominant role. As another example I may instance the importance of the 200-ft. Platform of southern England. Before the major ice-sheets deployed in this region it had been reduced over wide areas to a gently undulating plain of which the surface now stands at 200–250 ft. O.D. [4]. It was over this surface that much of the glacial drift was spread, and where the cover exists the old plain is literally beneath the notice of the soil surveyor. South of the Thames, however, it gathered no drift cover except in the neighbourhood of rising ground, where rain-wash or rock-rubble may mask it. It survives thus, drift-free, over much of the Western Weald, where it has been cut into by later stream dissection. It is conspicuous on the Weald Clay of west Sussex and the neighbouring parts of Surrey. Here the soil series, yet to be worked out, will reflect the occasional presence and importance of subordinate sandstone and limestone beds within the clay, but it will prove, I believe, even more important to distinguish the low, flat summit areas which represent the old plain and where leaching has been much longer continued than on other parts of the outcrop.

What is essential is that there should be recognition by the soil surveyor that such surfaces are as real and as mappable as geological outcrops. No doubt it is incumbent upon geomorphologists to map them, but once their existence is known they are easily recognized on the

ground. It will be found in many cases that, like rock outcrops, they coincide with a soil series, or a group of related soil series, and valid groupings so recognized would substantially help to generalize and clarify the almost intolerable burden of local soil-series nomenclature.

In conclusion it may be remarked that it is not only the benches or platforms marking old erosion surfaces that come within the purview of the geomorphologist. Scarp-faces and valley-sides and floors are also *surfaces* in active development during the current cycle of erosion and objects of interest to both the pedologist and the geomorphologist. The latter is in course of revising his ideas on slope-formation, having realized, in the words of Professor Kirk Bryan, that he has all too often in the past 'substituted words for knowledge and phrases for critical observation'. The question at issue is whether, as W. M. Davis assumed, slopes flatten with age or whether, as Walther Penck contended, they in general show 'parallel retreat'. The former view has commonly been received as axiomatic, but it is clear that, certainly in arid and humid tropical climates, possibly also under temperate conditions, some measure of 'parallel retreat' is demonstrable [5]. Pedologists appear to adhere to the orthodox view, finding truncation on upper slopes and colluvial accumulation below. So far as these findings are genuine and well tested they enforce the older belief and strengthen the case of those geomorphologists who seek to maintain the 'Davisian' view. There can, indeed, be no doubt that under some conditions slopes veritably develop by wasting of the shoulder and building up at the toe, but enough is known to make it certain that this is not the invariable rule, and it must not be generally assumed.

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THE ASSOCIATION OR HYDROLOGIC SEQUENCE IN CERTAIN SOILS OF THE PODZOLIC ZONE OF NORTH-EAST SCOTLAND

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DURING a detailed survey in 1938–42 on a scale of 6 in. to 1 mile in Aberdeenshire [4] in which the parent material is boulder clay derived from basic igneous rocks, a regular sequence of profiles was observed in passing from dry to wet conditions. These observations have been subsequently confirmed in a reconnaissance survey on a scale of $2\frac{1}{2}$ in. to 1 mile, which was extended over the whole county—an area of approximately 2,000 square miles.

From the original observations, in which a system of classification based on the hydrologic sequence was found to be most suitable, it was possible to establish on a given parent material certain major profiles [1] or associates which differed mainly in the matter of drainage, and to group these into a number of associations of different geological parent materials. Each association may possess a similar range of major profiles, but may differ in the incidence or dominance of certain associates. (Following common usage the word 'drainage' is used to express the hydrologic condition of the soil.)

The purpose of this paper is to point out the usefulness of this concept in soil classification, to describe the different major profiles (or associates of an association) as these occur in a region of soils resembling those of the Brown Podzolic Zone, and to indicate the trends and differences in these major profiles that have appeared as a result of laboratory investigation.

Milne [7, 7*a*] used the term 'catena' to describe certain 'rhythmic patterns related to land form' and pointed out that climatic as well as geological catenas are possible. His suggestion, however, of the catena as a genetic unit composed of soils differing only in drainage characters has had a great effect on soil-survey work throughout the world. A more or less similar concept has been used by Ellis [3] in Manitoba since about 1928, as a result of a suggestion by Nikiforoff, and it is this system which has been applied to Scottish soil survey. The catena concept has been used in the mapping and classification of soils in Australia [2] and Scotland [4], as well as in Africa and Canada. Bushnell [1] and Thomas [9] in the United States have stressed the usefulness of the catena for showing the relationship between hydrologic types, for forecasting so far unrecognized series, and for preventing confusion in the identification of superficially similar profile types.

The Association as a Taxonomic Group

The association as used in this paper is a group of soils which differ mainly in their hydrologic properties—that is, they are developed on the

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same parent material within one climatic area and represent the range of profile types which are produced as a result of differences in drainage. Naturally the range from the thin, shallow, excessively drained soils of the steeper slopes to the peaty gley soils of the depression is covered in a continuous sequence showing no abrupt transitions in the field. For the purpose of mapping this range is divided by defining certain major profiles and defining the range covered by each of these major profile types. In detailed mapping as many as seven or more major profiles may be separated, while for reconnaissance mapping the range is divided into fewer units.

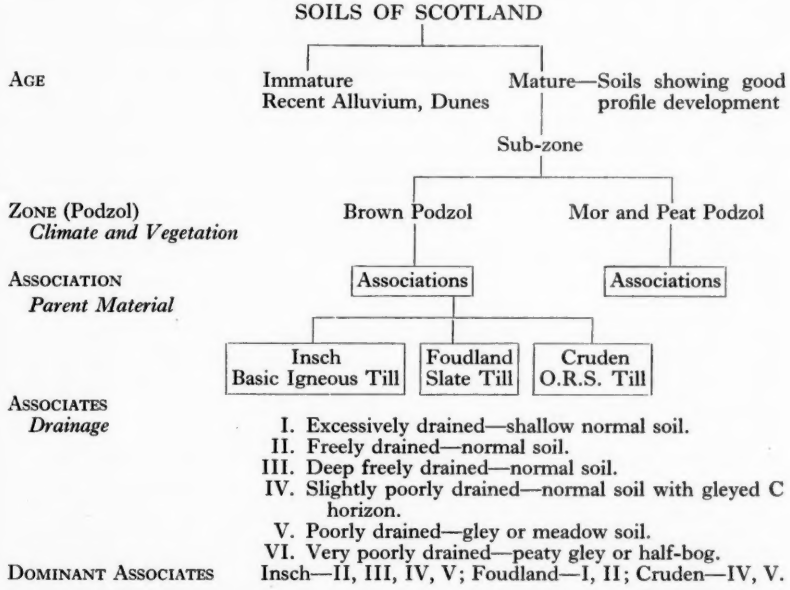
The adoption and continued use of the association concept in soil survey demonstrates that it has a useful and necessary place in bringing order into the study of the genesis and distribution of soils. Some opposition has been expressed [6] to its use as a genetic classification unit, since it is considered to cut across the recognized taxonomic groups. However, as Bushnell has pointed out, since the major profiles of a catena are related by being the units of the hydrologic sequence, it is quite justifiable to use the catena or association as one of the groupings in a scheme of classification. At any rate, the generally accepted systems of classification can be readily adapted to absorb the concept of the association, or catena, as an integral part.

Since the associates or major profiles of the association are related through their hydrologic sequence, and since the well-drained soils in the field may have areas of poorly drained and perhaps excessively drained soils associated with them, we are led inevitably to the idea that the soil climatic zone is characterized not merely by the well-drained so-called 'normal' soil, but by the complete range of hydrologic types in the association—that is, for every parent material the zonal character is expressed by the zonal association rather than by only one profile of the association, and each association shows correlated variations in its associates. This implies that on a range of soils on one parent material the soil profiles reflect both the nature of the climatic soil zone and the hydrologic conditions. It is hardly necessary to point out that at least in regions of moderate rainfall the characteristics determined by the climatic soil zone and parent material are most strongly expressed in the well-drained soils, while in the poorly drained soils the characteristics imparted by the hydrologic conditions are more strongly expressed. Nevertheless, each soil type is a result of the interaction of climate, parent material, and drainage through a certain period of time, and no one factor is of sole importance. Thus the peaty gley or 'half-bog' soils of different climatic zones—for instance, of the podzol zone as against the arid chestnut zone—do show differences due to the climatic influence, but these are less notable than similarities due to the hydrologic influence.

In the soil survey of Scotland it has been considered that the fundamental units of classification (series or associates, using Ellis's terminology [3], as we do in Scotland) are most logically arranged into groups representing the association, which includes the different major profiles developed on a particular type of parent material. Thus if the parent

material changes so as to produce significantly different soils under similar hydrologic conditions, the new soils would be grouped as a different association. Similarly the association only includes soils developed in one climatic soil zone, since each climatic soil zone has a different group of major profiles comprising the association. Therefore the associations in which the hydrologic range is similarly expressed, grouped together, comprise the soil zone. At the highest level of all the soils showing relatively full and stable profile development are grouped together as more or less mature soils, while the immature (azonal) soils form a second group.

This taxonomic arrangement is presented below.



Such a scheme has several advantages over more conventional classifications. From our experience it merits greater consideration than has been implied by Hills [5], who proposed a somewhat similar plan to be used merely as a convenience in the arrangement of mapping units.

So far the proposed scheme of classification has provided a pigeonhole for every type of arable soil we have found in the brown podzol zone of Aberdeenshire. Since the scheme employs a logical subdivision based on the factors that are accepted as being of prime importance in soil development, namely, age, climate and vegetation, parent material, and drainage, it should be possible to adapt such a classification scheme to the soils of any area by making adequate allowance for the importance of each of these factors in any particular case. Suitable additional groupings under any or all of the necessary categories can be added whenever necessary. This flexibility is a most valuable attribute.

Under the age differentiation, additional subdivisions may be made to accommodate soils of different geologic ages such as the few strongly developed podzols in southern Britain which have been inherited from a preglacial or interglacial period, or, as in the central and mid-western United States, where tills of different Ice Ages have been undergoing soil development since the time they were laid down.

Under parent-material differentiation, any parent materials (or mixtures and modifications of geological types) which give rise to significantly different soils can be included as new associations.

Under the hydrologic separation, any additional major profiles that occur under special hydrologic conditions may be added—for instance, in Scotland on fairly steep hill-slopes with an organic surface a number of types can be recognized which are due to the action of excess surface water in producing gleyed surface layers with apparently freely drained subsoils [8]—these will be added as a branch of the association at the wet end of the hydrologic sequence within the mor and peaty-podzol soil zone. The list of major profiles in the association may be enlarged to any required length depending on the number of different hydrologic types identified. In detailed work Bushnell [1] shows ten major profiles in Indiana, in Scotland seven have been used [4], while in reconnaissance work the list is shortened to four. An advantage of some importance in reconnaissance mapping follows the use of the hydrologic grouping, since each association can be represented on the map by a uniform colour on which the associates are distinguished by hatching. The intimate mixture of drainage types that is too complex to map out as individual major profile types can at least be indicated as part of the association rather than shown as a complex, which too often is simply an amorphous group in series mapping.

It will be noticed that names are given to the groups of soils at the association level—e.g. Insch Association (on basic igneous till in the brown podzolic subzone). In this way each parent-material type forming one association within one subzone has a separate name, and the individual soil types (associates or series) are described either as Insch I, II, IV, &c., or as Insch excessively drained, freely drained, and slightly impeded. Such a scheme has important advantages, as has been frequently pointed out [1, 3, 7], in avoiding the onerous burden of names that any extensive survey involves when names are given at the series level.

'Intrazonal' soils have no place as a group in the proposed scheme of classification. The poorly drained 'intrazonal' soils are, of course, an integral part of the association. Those 'intrazonal' soils strongly influenced by their parent material would be treated in a different manner. Soils developed on highly calcareous parent material would no doubt show a somewhat different hydrologic sequence from the less base-rich parent materials. If the hydrologic sequence is similar in the calcareous to the less base-rich soils, it would be apparent that the calcareous soils belonged to the same climatic soil zone, and the association developed on this parent material would be regarded simply as another interaction of parent material and climate. However, the hydrologic sequence on

calcareous parent materials usually shows a notably different set of major profiles.

The saline soils, solonchak, solonetz, and solod (with which the writers have some acquaintance), can be treated as major profiles of the association developing on saline parent materials under arid and semi-arid conditions. Different associations developed on parent materials of differing salinity will show the development of the various saline soils to different degrees in the hydrologic sequence of each particular association, so that some associations will show saline associates only in the terminal profiles of the wet end of the sequence, while the associates of other associations will be predominantly saline.

In grouping soils in this manner due emphasis is laid on the interrelationship of all the factors of soil formation rather than on the importance of only one factor (drainage or parent material) in the development of soils. In this way the similarities rather than the differences between hydrologic types and between soils of different parent materials are emphasized. It must be stressed that in using the association as a basis for soil classification the identification of the soil type is still strictly based upon the individual soil profile. By careful examination of hydrologic sequences and the characteristics imposed by different parent materials it has been possible to relate the characters observed in the field to particular combinations of the major factors in soil formation, namely, climate (which controls vegetation), parent material, and drainage.

By first arranging the individual soil types into groups which include all the hydrologic types on one parent material, the associations are defined. The associations showing similar major profile sequences are grouped together to define the soils of the various climatic soil zones. These groups, together with the immature soils, have been found to classify adequately the soils of north-eastern Scotland within the brown podzolic subzone.

In north-east Scotland two broad divisions of the podzol zone can be made:

1. Over much of the lower ground under moderately base-rich parent materials, soils such as those subsequently described are found. The pre-cultural vegetation of this area was probably deciduous forest, in which slightly podzolized soils with a mull humus occurred. As a result of cultivation the surface horizons of these soils have been changed and a grassy vegetation has taken its place which has probably increased the organic content of the present A horizon.

2. On light-textured parent materials such as quartz grit, quartzite, and granite, on the low ground as well as at higher elevations, a different set of profile types is found. These are characterized by a high organic accumulation of mor humus at the soil surface whilst an iron pan occurs under the A_2 horizon; the C horizon is freely drained. These soils are now becoming gleyed above the pan since the drainage is diverted laterally through the horizons above the iron pan. In this region, which we have termed the mor and peaty podzol sub-zone, there is also a relative absence of true gley or meadow soil types. The pre-cultural vegetation of this region appears to

have been different from that of the former, having been calluna heath and moor, with local pine and birch forest.

The Major Profiles of the Zonal Association in the Brown Podzolic Zone in North-east Scotland

The sequence of soils described below varies around six major profiles. Under favourable topographical conditions one hill-slope may have a continuous and complete range of all six of these profiles, but elsewhere, where there may be topographical irregularities either of the soil or of the underlying rock, there may be more than one repetition of the whole or part of the particular sequence. Thus it is obvious that on one parent material, dependent on the nature of the parent material and the topography, all or only certain of the major profiles may be found. It should be borne in mind also that under certain topographical conditions only one associate of an association might occur, thus giving a monotype association. While this condition is not common in glaciated regions it is probable that it is more general in unglaciated country. The following generalized descriptions indicate the chief morphological characters of the major profiles of the soil associations of the north-east of Scotland.

Major Profile I. Excessively drained

(*Uncultivated*)

0–6 in.—A horizon—organic surface of raw humus underlain by 2 in. of intensely black, highly organic mineral soil showing at the lower limit of the horizon a weakly developed bleached A_2 which may be absent.

6–14 in.—B horizon—yellowish-brown zone of accumulation, friable with weak crumb structure; passing into a greyer compact indurated layer at about 10 in., and merging below 14 in. into the thin stony uniformly coloured parent material, which may range from light loam to clay loam.

(*Cultivated*)

When cultivated this soil has a dark-brown surface horizon of 5–7 in. of loamy sand to stony sandy loam texture. The B horizon is generally shallower than that described in the uncultivated profile, due to its partial inclusion in the plough layer.

II. *Freely drained*

0–9 in.—A horizon—brown, friable, with soft crumb structure, loam to light loam.

9–24 in.—B horizon—yellow-brown, friable with weak crumb structure; changing sharply at about 16 in. into a greyer compact indurated layer of a somewhat lighter texture, and merging at 24 in. into the uniformly coloured stony parent material.

III. *Deep freely drained*

0–9 in.—30 in.—A horizon as II, except for greater depth and less stony nature.

9–30 in. and over—as II.

This soil may owe its special character in part to colluvial action or to crag and tail effect of glaciation, to its south-eastern exposure, or to long cultivation, being former 'infield' land of earlier agricultural times.

IV. *Slightly impeded drainage*

0–9 in.—A horizon—as II.

9–24 in.—B horizon—yellow-brown friable loam to light loam, with some iron and organic mottling and greyer colours appearing at about 16 in. and increasing with depth, and becoming weakly cloddy at depth. Below 24 in., passing into more or less gleyed parent material.

V. *Poorly drained*

0–9 in.—A horizon—grey-brown cloddy heavy loam to clay loam, lower in organic matter than the preceding profiles.

9–24 in.—G horizon—changing through 2 in. into iron-stained clay loam; structure consisting of grey-coated, cloddy, acutely angled prismatic elements of about 3 in. per side, with brown and yellow colours in the interior of the clods. Below 24 in. the structure disappears in strongly gleyed massive plastic parent material, with many rotten rock fragments.

VI. *Very poorly drained* (*peaty gley*)

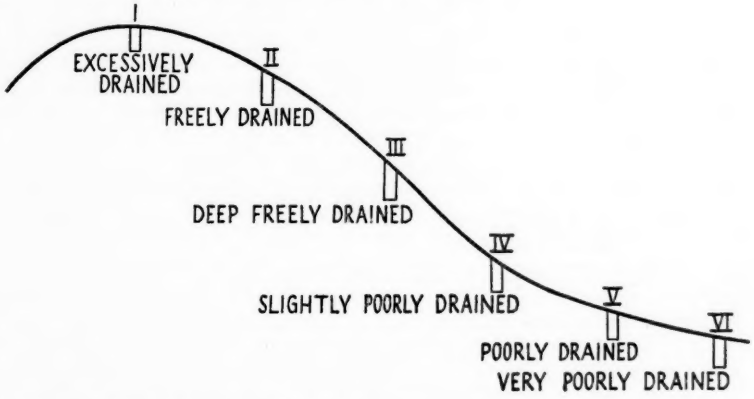
0–8 in./18 in.—A horizon—highly organic loam.

8–18 in.+ —G horizon—changing sharply into strongly cloddy plastic grey to blue-grey clay loam, with some iron staining in the upper limits, and blue colours appearing at the level of the water-table; showing iron stains around root channels.

In still wetter positions deeper peat accumulations occur; however, up to the present no differentiation of these has been attempted.

It will be recognized from the profile descriptions that an uncultivated example of Profile I has been described, while cultivated soils provide the other examples. This is the usual state of affairs in Aberdeenshire where the shallow soils on rougher, steeper slopes have not generally been cleared for arable agriculture.

A diagrammatic representation of the various major profiles in the zonal association, as an example of the way the sequence occurs when controlled by topography, is presented below.



As a result of laboratory investigations certain trends characteristic of each major profile type, and variations from one profile type to another, have become evident, so that on the basis of field recognition of the major profile it is possible to predict some of the important chemical characteristics of the soils.

The Association and Soil Organic Matter

Experience with the hydrologic sequence in the field indicated that the amount of organic matter in the different major profiles varies regularly from the dry to the wet end of the association, with high levels

at both ends (I and VI) and a minimum in V. A study of this variation, involving 128 profiles on 8 different parent materials, has demonstrated this regular trend, shown in Table 1.

TABLE 1

Nitrogen Levels in the Major Profiles of the Association

	Excessively drained	*Freely drained*	*Deep freely drained*	*Slightly impeded*	*Poorly drained*	*Peaty gley*
Major Profile . .	I	II	III	IV	V	VI
% nitrogen in surface horizons . . .	0·72	0·34	0·33	0·27	0·26	0·50
N in A horizon as 1,000 lb./ac. . . .	12·0	8·7	13·3	7·2	6·4	11·0
Approx. depth . .	7 in.	10 in.	16 in.	10 in.	10 in.	9 in.
No. of profiles . .	15	42	9	17	38	7

The nitrogen percentages illustrate the trend from high amounts of organic matter in both the dry and wet ends of the hydrologic sequence, with lower values in the freely drained soils and still lower in those subjected to a fluctuating ground-water table. The actual amount of nitrogen present per acre

i.e. $$\frac{\%\ \text{N} \times \text{depth in inches} \times 2{,}000{,}000}{800}$$

falls off from the excessively drained (I) to the freely drained (II) with an increase again in the deep freely drained (III) because of its great depth of A horizon—16 in. In the second 8 in. of this profile the nitrogen content is only slightly lower than that of the first 8 in. There is a decrease to a minimum in the poorly drained (V) before the increase again in the peaty gley (VI). The percentage nitrogen in this soil (VI) is variable, being dependent on the amount and depth of the organic matter present; it may greatly exceed the figures given in Table 1. The low values for both nitrogen percentage and nitrogen per acre shown for Major Profile V is probably connected with more favourable conditions for microbiological decomposition by virtue of the fluctuating water-table, higher pH, and base status. In contrast, the high values in Profiles I and VI are no doubt due to less favourable conditions for decomposition, being too acid and dry in I and too acid and excessively wet in VI. An examination of the organic matter in a number of soils of the Insch Association showed that there is a somewhat higher content of wax and lignin in the poorly drained soils. Since these substances are more resistant to decomposition, it is thought that an increase in their amounts is correlated with greater biological activity.

The Association and Soil Phosphorus

In routine analysis for total phosphorus in soil-survey samples the well-drained soils show a gradual decrease in total phosphorus with depth—in general decreasing steadily to about 50 per cent. of the surface

figure in the C horizon. In contrast, the poorly drained types (Major Profile V) show a sudden decrease in the total phosphorus in the G_1 horizon where mottling is evident, and where the value reaches the lowest level in the profile. The total phosphorus rises again in the parent material. In addition, the percentage of phosphorus in the poorly drained (V) soil is markedly less than in the well-drained types (I, II, and III).

An example is given below:

TABLE 2

Total Phosphorus in a Well-drained and a Poorly Drained Profile

Foudland Association (boulder clay from slate)

Major Profile II		*Major Profile V*	
Depth (cm.)	% P_2O_5	*Depth (cm.)*	% P_2O_5
0–15	0·28	0–20	0·19
20–5	0·21	30–40	0·09
40–50	0·17	55–65	0·12
60–70	0·16	80–90	0·13

These two profiles were taken from the same field and presumably received the same manurial and cultural treatment. An examination of thirty-one pairs of contrasted profiles (i.e. Profile II and Profile V) with each pair taken in the same field to minimize cultural and parent material differences has been carried out, and the results are presented below:

TABLE 3

The Relative Amounts of Total Phosphorus in Two Contrasted Profiles

(Average of 31 profile pairs; surface of Major Profile II = 100)

	Relative amounts of total phosphorus	
	Major Profile II freely drained	*Major Profile V poorly drained*
Horizon 1	100	78
,, 2	73	42
,, 3	64	42

This striking reduction in the amount of total phosphorus present in the poorly drained soil, and especially in its upper gleyed horizons, is possibly related to the reducing conditions existing in the poorly drained V profile. There is also abundant analytical evidence (Table 4) indicating that a higher percentage of acetic soluble phosphorus occurs in the surface layers of V than II.

TABLE 4

Total and Acetic Soluble Phosphate in the Surface Layer (approx. 0–20 cm.) of the Freely Drained and Poorly Drained Associates

		Major Profile II		*Major Profile V*	
		Freely drained		*Poorly drained*	
Association	*Locality*	% P_2O_5 *total*	*Avail.* P_2O_5 *(mg.)*	% P_2O_5 *total*	*Avail.* P_2O_5 *(mg.)*
Tarves	Tillycorthie	0·31	6·5	0·18	8·8
,,	Drumwhindle Mains	0·28	2·6	0·24	5·7
,,	Cairnbrogie	0·37	3·8	0·21	5·8
,,	Pitgavenny	0·34	5·4	0·23	13·0
,,	Udny Castle	0·42	2·2	0·25	4·8
,,	Balquhain	0·34	2·2	0·29	10·0
Countesswells	Glen Tannar	0·21	1·3	0·22	6·2
,,	Cairntradlin	0·30	3·8	0·22	6·5
,,	Kilduthie, Craigton	0·28	5·9	0·24	7·2
Foudland	Ythanwells	0·28	2·5	0·19	4·5
,,	Greystone	0·32	3·5	0·17	7·3
Insch	Uppertown Glen—Buchat	0·37	2·4	0·33	5·4
,,	Pitellachie	0·39	3·7	0·33	4·2
,,	Easter Buchat	0·33	5·3	0·27	7·3
,,	Robieston	0·33	0·88	0·21	2·4

The above figures are selected data illustrating the tendency for acetic soluble phosphorus in the surface layer to be higher in the poorly drained associate than in the freely drained: exceptions do, of course, occur.

Amorphous Sesquioxides in a Well-drained and a Poorly Drained Profile

Tamm's acid oxalate extract removes a larger amount of 'free' Fe_2O_3 and Al_2O_3 from the surface layers of the freely drained soils, Major Profile II, than from the wet, Major Profile V, but in the basal layers removes more from V than from II. The results for two pairs of profiles are given below, and are typical of the trend obtained for many soils.

TABLE 5

Free Sesquioxides removed by Tamm's Acid Oxalate Extract

Tarves Association (Balquhain—mixed acid and basic igneous boulder clay)

Major Profile II			*Major Profile V*		
Depth (cm.)	% Fe_2O_3	% Al_2O_3	*Depth (cm.)*	% Fe_2O_3	% Al_2O_3
0–20	1·60	1·43	0–20	0·78	0·50
28–38	1·68	1·19	25–35	0·83	0·33
40–50	1·46	1·64	55–65	1·24	0·35
55–65	0·70	0·82	100–10	1·33	0·34
80–90	0·78	0·39	..	..	..
110–120	0·68	0·32	..	..	..

Tarves Association (Tillycorthie—mixed acid and basic igneous boulder clay)

Major Profile II			*Major Profile V*		
Depth (cm.)	% Fe_2O_3	% Al_2O_3	*Depth (cm.)*	% Fe_2O_3	% Al_2O_3
0–18	1·52	0·80	0–15	0·85	0·43
23–30	0·66	0·75	20–30	0·75	0·38
45–55	0·59	0·58	40–50	0·92	0·35
75–85	0·59	0·54	70–80	1·16	0·40
..	..	..	100–20	1·11	0·36

The fixation of phosphate is known to be related to the amount of free sesquioxides. It appears, therefore, that since the freely drained soils tend to have about twice as much 'free' Fe_2O_3 and Al_2O_3 in their surface layer as the poorly drained soils, they have a greater tendency to fix applied phosphate than the poorly drained soils. This is a partial explanation of the higher amount of total phosphate held in the surface layer of the freely drained soil.

Clay Ratios

The ratios of silica, iron oxide, and alumina in contrasted associates of the Insch Association indicate the nature of the variations between the different major profiles of the hydrologic sequence. In the example given (Table 6) the freely drained profile is contrasted with the poorly drained profile.

TABLE 6

Clay Ratios on Two Contrasted Major Profiles of the Brown Podzolic Zonal Association

(Insch Association—basic igneous boulder clay)

		$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
Major Profile II—freely drained					
A	0–10 cm.	2·62	4·15	7·2	1·73
	20–30 ,,	1·66	2·18	7·0	3·21
B_1	35–45 ,,	1·5	1·98	6·78	3·5
B_2	57–68 ,, indurated	1·61	2·0	8·3	4·16
C	105–10 ,,	2·38	3·17	9·45	2·98
Major Profile V—poorly drained					
A	0–5 cm.	2·74	4·31	9·6	4·03
G_1	30–5 ,,	2·14	2·89	8·02	2·78
G_2	50–60 ,,	1·94	3·25	4·72	1·45
G_3	60–75 ,,	2·69	3·51	11·6	3·31
G–C	115–20 ,,	4·10	7·91	3·31	1·08

The freely drained profile shows the weak podzolization of the brown podzolic soil sub-zone, and indicates primarily the translocation of iron and alumina to the B_1 horizon. The comparison of alumina with iron, however, shows the alumina to have travelled relatively farther than iron into the B_2 horizon where it is more concentrated. This is in agreement with Muir [8].

The poorly drained profile shows no regular trends in the clay ratios—the variations apparently occurring in a haphazard manner. SiO_2/Fe_2O_3

ratios varying between 2 and 20 [4] have been found in the poorly drained profiles. The fluctuating water-table with the attendant variations in oxidizing conditions is probably responsible. The rhythmic fluctuations of high to low—high to low that occur in the SiO_2/Fe_2O_3 may be a result of the water-table remaining at various levels for significant periods.

The Indurated Layer

In digging into the freely drained profiles (I, II, and III) the presence of a compact indurated layer (described here as B_2) is an obvious feature. It occurs below the yellow-brown zone of iron accumulation, and is greyer in colour than this layer. Pore-space determinations on this layer give values of about 20 per cent. as compared with around 50 per cent. for the layer above. Analysis shows it to have a much lower clay content than the layers above and below, and analysis of this clay fraction indicates an accumulation of alumina. The layer is absent in any profile showing signs of the action of excess ground water, that is, in IV, V, and VI. Typical examples are given in Table 7.

TABLE 7

The Indurated Layer of Freely Drained Profiles of the Brown Podzolic Zonal Association

(Insch Association—basic igneous boulder clay)

	Major Profile II		*Major Profile III*	
Horizon	*Clay* %	Al_2O_3/Fe_2O_3	*Clay* %	Al_2O_3/Fe_2O_3
B_1	21·7	3·2	17·1	2·5
B_2 indurated	8·2	4·16	12·8	4·3
C	18·1	2·98	21·0	2·7

This zone of compaction seems somewhat similar to that described for certain grey-brown podzolic soils in Kitsap County in the State of Washington in the United States [10].

pH, Base Saturation, and Exchange Capacity

While the trends in pH and base saturation tend to be obscured in arable soils by cultural operations, certain generalities can safely be made. Profile I (excessively drained) is strongly acid and highly unsaturated throughout, usually being as much as 90 per cent. unsaturated even in the C horizon. The exchange capacity is closely correlated with the organic matter, and consequently falls off rapidly with depth from the high surface values.

Profiles II and III (freely drained and deep freely drained) show the same tendencies, but there is a marked increase in pH and base saturation with increasing depth. The exchange capacity values decrease with the falling off of organic matter with depth and also show a marked decrease in the indurated B_2, accounted for in part by the low clay content. The C horizon in these soils usually is about 75 per cent. unsaturated.

The poorly drained profile V, since it receives drainage water from the surrounding well-drained soils, and is subject to less intense vertical leaching, has a higher pH and base status than the freely drained types, and is more highly saturated throughout. Because of its low organic matter content, the change in base exchange capacity with depth is less marked.

Profile IV (slightly impeded drainage), being transitional between the freely drained and poorly drained profiles, shows intermediate characteristics.

The peaty-gley soil (Major Profile VI) is usually strongly acid, and highly unsaturated, varying between 80 and 90 per cent. unsaturated in the organic surface and between 70 and 90 per cent. unsaturated below. The base exchange capacity of this type is, of course, very high in the surface organic layer, decreasing sharply in the mineral soil below.

A set of characteristic pH values are given for five of the six major profiles in Table 8.

TABLE 8

Variations in pH in the Major Profiles of Brown Podzolic Soils in Scotland

(Tarves Association—mixed acid and basic igneous boulder clay)

Horizon	*I*	*II*	*III*	*V*	*VI*
1	4·21	5·25	5·22	5·48	5·12
2	4·73	5·39	5·32	5·86	4·73
3	5·03	5·68	5·76	6·11	4·99
4	5·03	5·96	6·26	6·11	5·76
5	5·20	..	..	6·14	5·97
6	5·53	..	..	..	..

Profiles I to V inclusive were taken on one hill-slope within a total distance of about 500 yards, all being cultivated soils except I, which was under pine and heather. Profile VI was taken at another location on the same parent material. The variations in pH are typical of the medium acid parent material of the region.

Variations in Exchangeable Calcium and Magnesium in Major Profiles II and V

In its distribution down the profile of the freely drained associate the exchangeable calcium is generally highest in the A horizon; below this in the B_1 there is a sharp decrease; the B_2 shows a further decrease, while the C may show a rise or decrease, depending on the parent material. In the poorly drained soil (Major Profile V) exchangeable calcium is more uniformly distributed; generally there is a decrease in the G horizon below which the value remains constant or may rise considerably depending on the parent material. However, the amount in the G horizon is higher in this profile than in the B_1 and B_2 horizons of the freely drained soils.

Exchangeable magnesium in the freely drained soils decreases sharply from the A horizon downwards, rising slightly in the C horizon, while in the poorly drained soil (Major Profile V) the reverse is true; that is to say,

it increases sharply with depth to values very much higher than in the lower layers of the freely drained soil. This is in agreement with Zavalishin as recorded by Joffe [11]. Mitchell [13] has shown that magnesium is more easily displaced than calcium and is therefore more mobile than calcium in normal soils, and probably accumulates in the gley horizons as a result of the enrichment by drainage water from surrounding freely drained soils.

The trend is illustrated by a pair of profiles, freely drained and poorly drained, taken from the same field in the Foudland Association (slate boulder-clay) and has been observed in many comparative pairs of profiles over different parent materials within the brown podzolic subzone.

TABLE 9

Trends in the Distribution of Exchangeable Calcium and Magnesium

(m. eq. 100 g. soil)

	Freely drained Major Profile II				*Poorly drained Major Profile V*		
Horizon	Ca	Mg	Ca/Mg	*Horizon*	Ca	Mg	Ca/Mg
A	4·20	0·32	13·1	A	2·69	0·09	29·7
B_1	0·81	0·07	11·6	G	2·44	0·54	4·5
B_2	0·26	0·02	13·0	G	3·99	2·09	1·9
C	0·17	0·07	2·4	G	4·64	4·14	1·1

Parent Material and the Zonal Association

The major profiles of the zonal association illustrate the hydrologic sequence that is general in the brown podzolic soils. On different associations with different parent materials there are slightly different expressions of the hydrologic conditions—for instance, the Insch Association developed on basic igneous boulder clay tends to have richer brown colours, heavier textures, higher pH's, base saturations, and base exchange capacities throughout the various profiles than do soils on some of the more acidic, more easily leached, parent materials. Differences in the colours of the soils between different parent materials are quite marked—especially so in contrasting the freely drained soils derived from Old Red Sandstone with those from other more neutral-coloured parent materials. The textures of the soils are, of course, closely related to the parent material, and this in turn has a big effect on the relative frequency and distribution of the different major profile types occurring under similar topographic conditions.

There are, however, well-defined trends in the distribution of certain constituents and characteristics in the associates of an association, irrespective of parent material, and these trends are related to the degree of natural drainage of the soil.

Summary

An account has been given of a scheme of classification based on the association concept as used in the Scottish Soil Survey, with some discussion of its advantages and potentialities.

The variations in soil properties resulting from different hydrologic conditions in the associations in the brown podzolic soils of Scotland can be shown to follow definite trends from one major profile to another, irrespective of the parent material of the association. These variations are discussed with respect to the distribution of nitrogen, phosphorus, amorphous sesquioxides, sesquioxide translocation, the indurated layer, pH, base saturation, and base exchange capacity and exchangeable magnesium and calcium.

From the regularity of these trends it is suggested that the character of a soil zone is best described by reference to the zonal association, rather than by the characters of the normal freely drained soil, as is usually done.

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PODZOLIC SOILS OF WALES

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THE general tendency of soil development in Wales is towards a podzolic type of profile, yet well-developed podzols are exceptional. This is due partly to the effect of human interference, partly to the character of the parent materials, and partly to the strong surface relief. In the present paper we shall attempt to describe some of the principal variants of the podzol profile found in Wales. The conditions governing soil development will first be briefly outlined.

Geology and Relief

The country is generally mountainous or hilly, rising to 1,079 metres in Yr Wyddfa (Snowdon). Apart from comparatively small areas of alluvium and coastal flats, there is little level ground. The surface varies from the sharply defined features of the mountain regions to the rolling or undulating country of the foothills and lowlands.

The greater part of Wales is formed of hard non-calcareous sedimentary rocks of Cambrian, Ordovician, and Silurian age. Crystalline metamorphic rocks (Pre-Cambrian) and igneous rocks (mainly Ordovician) occur in the north-west and extreme west. Old Red Sandstone (Devonian) and Carboniferous, including Carboniferous Limestone, occur in the south and north-east. There are small areas of Trias in the north and south and of Lower Lias in the south.

The whole of the country has been subjected to glaciation and most of the lowland area carries a mantle of drift, comprising boulder clay and derived sands and gravels. Over much of the country this mantle is of inconsiderable thickness, and generally reflects the character of the subjacent or adjacent rocks. Colluvial material (hillwash) commonly occurs at the foot of slopes.

Welsh soils are thus formed typically from hard non-calcareous rocks or their debris. They are essentially soils of primary weathering, for the Palaeozoic sediments that form such a large part of the country have generally undergone considerable alteration and are mainly formed of crystalline or sub-crystalline material. Certain Silurian rocks in mid-Wales, and some Carboniferous rocks in which the original sedimentary character has survived, form exceptions. In such cases, the derived soils are of secondary weathering.

Quartzose sands are comparatively infrequent, apart from dune areas, where the derived soils are very immature. This contributes to the scarcity of well-developed podzol profiles in such a humid climate as Wales.

Climate

The climate is oceanic, with mild winters and cool summers. The rainfall is closely related to surface relief and varies from about 650 mm. per annum in certain flat coastal areas to about 5,000 mm. under the

peak of Snowdon. These are extremes, and over most of the country the annual rainfall varies between 1,000 and 2,000 mm.

In the western coastal regions the mean temperature is about 5° C. for January and 15° C. for July. Farther east the extremes are rather more marked. There is, of course, a fall in temperature with elevation. Although frost may occur from time to time during the winter, it is rarely severe or of long duration, particularly in the west. From the soil-forming standpoint the climate is practically frost-free, except in the higher mountains. Snowfall is exceptional in the maritime lowlands and not frequent inland, except at high altitudes.

The wetness of the climate is more marked than would appear from the rainfall figures since rain is fairly uniformly distributed throughout the year and the atmosphere generally shows a high percentage humidity.

Vegetation and Cropping

The upper limit of cultivation varies from about 200 metres in Caernarvonshire to nearly 400 metres in central Wales. In the period preceding the Roman occupation the vegetation in well-drained situations was mainly deciduous forest (*Quercetum petraeae*) up to about 500 metres, but little of this primitive forest now survives. The poorly drained areas in the lowlands were partly in wet woodland and partly in marsh or swamp vegetation. Most of the well-drained soils and a considerable proportion of the poorly drained soils are now in agricultural use. The uncultivated upland at the present day is mainly acidic grassland, heath, moorland, and mountain. An increasing area is being planted to coniferous forest by the Forestry Commission. Land under crops and grass forms about 54 per cent. of the total area.

Agriculturally, Wales is predominantly a grassland country. In the years immediately preceding the 1939–45 war, arable land formed a little over 20 per cent. of the agricultural area. At present the proportion is a little over 30 per cent. Typically the land is under the plough for 3 or 4 years* and is then in grass for 5, 6, or even more years. The principal grain crop is oats. The grassland character is impressed even on soils actually in arable cultivation. Outside the agricultural lands, the rough grazings and wastes are also mainly of the grassland type.

Podzols

As stated above, well-developed podzols are uncommon in Wales partly because of the lack of parent rocks, such as quartzose sands or quartzites, poor in bases, and partly because the whole of the country has been subjected to interference through deforestation, grazing, or cultivation. The grassland character impressed on Welsh soils has already been noted. It should be remembered also that the forest or scrub that covered most of the country in primitive times was deciduous and, therefore, not likely to be associated with extreme podzolization.

* Under war conditions two or more cereal crops may be taken after ploughing up from grass. There has been a considerable increase in the areas of wheat and barley, but oats remains still the principal cereal crop.

At the present day the best-developed podzols are formed under heath vegetation, which may have replaced former deciduous forest. Profile I from Esclusham, near Wrexham, Denbighshire, may serve as an example. It is developed over weathered Millstone Grit (a coarse quartzose grit) at 300 metres under a mean annual rainfall of about 1,100 mm. The vegetation is mainly *Calluna vulgaris* and *Festuca* spp. The following is the field description:

Horizon	*Depth (cm.)*	*Description*
A_0 / A_1	0–23	Raw humus layer. Org. C 40·7%; pH 3·3.
A_2	23–38·5	Grey sandy loam, loose. Org. C 5·9%; pH 3·24; Si/Al 2·54; Si/R 2·42.
B	38·5–54	Reddish-brown light loam; more compact. Org. C 5·2%; pH 3·76; Si/Al 2·30; Si/R 1·75.
B (C)	54+	Lighter brown rubbly light loam passing to rock. Org. C 1·8%; pH 4·14; Si/Al 2·30; Si/R 1·72.

The data do not show any humus accumulation in the B horizon. It is possible, however, that with closer subdivision a humus B horizon might have been distinguished, since the fall in organic-carbon content from A_2 to B is comparatively small, whilst that from B to B (C) is very marked. This profile shows a feature very common in Welsh soils, namely, the extension of the soil profile into the parent rock. Yellowish-brown loamy material is found in rock fissures down to a metre or more, whilst brown staining can be seen for some metres below this in exposed rock surfaces.

The molecular ratios of the clay fractions show clearly the contrast between the A and the B horizons and suggest that in this case podzolization consists mainly in a leaching and deposition of iron oxides. The small differences between the figures for the B and the B (C) horizons suggest that they are practically identical in character.

The extreme acidity in the first three horizons should be noted. It is due in part to the presence of sulphuric acid from the biological oxidation of sulphur compounds. Extraction of the A_{0-1} horizon material with water yielded 0·098 per cent. of sulphuric acid.

A small accumulation of humus in the B horizon is shown in Profile II from Cefn-y-Bryn, west Glamorgan. It is developed in a quartzose conglomerate of Old Red Sandstone (Devonian) age. The altitude is 100 metres and the mean annual rainfall 1,000 mm. The vegetation is *Ulex* spp. and *Festuca* spp. The following is the field description:

Horizon	*Depth (cm.)*	*Description*
A_0 / A_1	0–10	Fibrous raw humus layer.
A_2	10–18	Greyish sand, loose. Org. C 1·61%; pH 4·6; Si/Al 3·70; Si/R 3·33.
B_1	18–28	Reddish-brown sandy loam, somewhat compact. Org. C 2·08%; pH 4·7; Si/Al 2·44; Si/R 1·67.
B_2–C	28–41	Yellowish-brown sandy loam passing to shattered rock. Org. C 0·48%; Si/Al 2·80; Si/R 2·03.

The organic carbon figure for the raw-humus layer was not determined, but as this is almost pure organic matter it would probably be over 40 per cent. The rise in organic carbon from the A_2 to the B is not a common feature in Welsh podzols, although it is common in English podzols on sandy parent materials. The C character of the lowest horizon is suggested by the rise in SiO_2/R_2O_3 ratio. As in the Esclusham profile, the leaching affects principally the iron oxides, although in this profile there is evidence of movement of alumina. In neither profile is there any suggestion of ortstein development.

Humus B horizons have been seen in certain profiles in Anglesey developed in brashy quartzitic colluvium. They are much contorted and disturbed by downward slip, and no detailed examinations supported by analytical determinations have been made.

The commonest type of podzol in Wales is a shallow iron podzol developed from hard Palaeozoic sedimentary rock, principally shales. Profile III, from Minffordd, Ponterwyd, Cardiganshire, is typical. It is developed in Ordovician shale at about 220 metres elevation under a mean annual rainfall of about 1,150 mm. with heath vegetation (*Calluna vulgaris*, *Festuca* spp., &c.).

The field description is as follows:

Horizon	*Depth (cm.)*	*Description*
A_{0-1}	0–15	Blackish-brown loamy raw humus. Org. C 34·6%; pH 4·1; Si/Al 2·51; Si/R 2·43.
A_2	15–23	Grey-mottled, slightly peaty silt loam. Org. C 8·0%; pH 4·1; Si/Al 2·48; Si/R 2·33.
B_2	23–4	Rusty medium loam slightly indurated (ortstein). Org. C 4·6%; pH 4·3; Si/Al 2·33; Si/R 1·69.
B_3	24–30	Reddish-brown shaly medium loam. Org. C 3·2%; pH 4·2; Si/Al 2·14; Si/R 1·78.
B_3–C	30+	Reddish-brown shaly light loam in rock brash, passing to rock. Org. C 2·6%; pH 4·5; Si/Al 2·01; Si/R 1·59.

The gradual decrease in organic carbon down the profile, with the absence of any suggestion of a B_1 horizon, may be noted. The figures for the clay fraction show the intense eluviation of iron from the top horizons. The thin layer of ortstein character is markedly ferruginous.

Gley-podzolic Soils and Peat Podzols

Podzols are essentially soils of free drainage. The development of the B horizon, however, can result in drainage impedance, thereby giving a new direction to the development of the profile, culminating in the formation of peat soils.

The first example of this line of development is one in which impedance in the B horizon has not greatly modified the general podzol character. The soil in question, Profile IV, occurs near Pentre Voelas, Denbighshire, at about 400 metres under a mean annual rainfall of about 1,250 mm. The parent material is gravelly boulder clay, mainly Ordovician hard shale and grit. The vegetation is dominated by *Nardus stricta* with *Galium saxatile*, occasional *Holcus* spp. and rushes.

The following are the field characters:

Horizon	*Depth (cm.)*	*Description*
A_{0-1}	0–15	Black, mainly amorphous but locally fibrous, peat. pH 3·9.
A_2	15–25	Grey silty loam to heavy loam, rather stony, some rusty mottling. Org. C 1·96%; pH 4·2; Si/Al 2·51; Si/R 2·40.
B_{1-2}	25–56	Reddish or yellowish brown gritty and stony heavy loam with thin ortstein development at upper limit. Compact. Org. C 4·48%; pH 4·4; Si/Al 2·10; Si/R 1·60.
B_3–C	56–88	Greyish-brown gritty and stony silt loam. Org. C 0·58%; pH 4·6; Si/Al 2·44; Si/R 2·00.
C	88+	Light grey gritty and stony medium to heavy silt loam. Org. C 0·32%; pH 4·8; Si/Al 2·32; Si/R 1·98.

Although no marked B_1 horizon was distinguishable, the horizon B_{1-2} contains considerably more organic matter, as shown by the organic-carbon figure, than the A_2 horizon. A sharp fall in organic-carbon content in the next horizon probably reflects the absence of root penetration consequent on compaction and drainage impedance. The figures indicate a slightly less acid reaction than in freely drained iron podzols. The molecular ratios for the clay fraction indicate the leaching of sesquioxides, particularly ferric oxide, from the A horizons. Finally, the marked development of peat and the presence of rushes in the herbage indicate moist conditions. It may be supposed that the podzolic character was developed under an earlier heath vegetation with free drainage.

In the next example the impedance is more marked and the gley character more pronounced. Profile V occurs at Hafod Lon, Abererch, Caernarvonshire, at about 60 metres with fairly level topography under a mean annual rainfall of about 1,000 mm. The parent material is boulder clay of mixed igneous and shale origin. The vegetation is poor wet grassland, probably reclaimed from shallow peat many years ago and since allowed to deteriorate.

The following are the profile data:

Horizon	*Depth (cm.)*	*Description*
I*	0–15	Dark brownish-grey mottled peaty silt loam. Org. C 12·2%; pH 4·7; Si/Al 2·59; Si/R 2·29.
II	15–23	Light grey with pale brown mottlings, silty loam with humus streaks. Org. C 3·1%; pH 4·2; Si/Al 2·49; Si/R 2·42.
III	23–41	Slightly yellowish-grey with dark brown or almost black peaty bands. Peaty silt loam. Org. C 3·9%; pH 4·3; Si/Al 2·34; Si/R 2·08.
IV	41–62	Pale brownish-grey heavily rust-brown mottled silt loam. Org. C 0·5%; pH 4·6; Si/Al 2·26; Si/R 1·72.
V	62+	Slightly paler with less iron stain than preceding layer. Heavy silt loam. Org. C 0·3%; pH 4·8; Si/Al 2·53; Si/R 2·00.

* As there is some doubt with regard to the applicability of the conventional horizon nomenclature in this case, we have preferred simply to number the horizons. I and II are probably A horizons, III has mixed A and B characters, in IV the G character is evident. V is C with some G character.

The organic content of the upper horizons has probably been considerably diminished owing to reclamation from waste. The sharp fall in organic carbon at 41 cm. may be noted. This probably represents the restriction of root development by wetness. The Al_2O_3/Fe_2O_3 ratios indicate an intense removal of iron from the upper horizons. The development of the B (G) horizon is not so strongly marked. Presumably there has been considerable lateral translocation of iron. The pH values are low, as in podzols, whereas in true gley soils rather higher figures are found.

Peat podzols occur widely throughout the mountainous regions of north Wales. The following example, Profile VI, occurs at Foel Fras, Caernarvonshire, at about 1,000 metres under a mean annual rainfall of at least 2,500 mm. The parent material is weathered acid igneous rock (felsite). The vegetation is *Juncus squarrosus*, *Calluna vulgaris*, *Molinia coerulea*, *Nardus stricta*, mosses, &c.

The profile consists of:

Horizon	*Depth (cm.)*	*Description*
A_{0-1}	0–92	Dark brown wet fibrous peat.
A_2	92–102	Grey silty loam with bleached gravel. Org. C 3·0%; pH 3·9; Si/Al 2·42; Si/R 2·13.
B	102–110	Rusty brown gravelly loam, intensity of colour increasing with depth, passing to shattered rock. Org. C 2·2%; pH 4·5; Si/Al 1·19; Si/R 0·75.

The strong development of the peat horizon may be noted. The B horizon extends into the shattered rock. In other examples the B horizon is entirely within the rock, the upper portion of which is bleached.

Podzolic Gley Soils

This term may be applied to soils which have developed throughout under conditions of impeded drainage, but which also show podzolic characters. They are distinct from gley-podzolic soils, in which gleying may be presumed to have succeeded an earlier podzolic phase with free drainage, and also from typical gley soils, where there is no marked differentiation affecting the clay fraction.

This group may be illustrated by Profile VII at Caerau, Dinas, west Caernarvonshire. It is developed at about 80 metres on a slight northerly slope under a mean annual rainfall of rather less than 1,000 mm. The vegetation is poor grassland with sedges, rushes, and occasional *Calluna vulgaris*. The parent material is a fairly stoneless boulder clay, mainly of Carboniferous Limestone material, but deeply decalcified. The field description is as follows:

Horizon	*Depth (cm.)*	*Description*
A	0–13	Dark brownish-grey fine sandy loam, with rusty markings along root channels. Org. C 4·6%; Si/Al 3·00; Si/R 2·44.
B (G)	13–33	Greyish ground colour with abundant yellowish-brown mottlings and patches. MnO_2 concretions. Medium to heavy loam. Org. C 2·0%; Si/Al 2·62; Si/R 1·90.

Horizon	*Depth (cm.)*	*Description*
G	33–92	Grey heavy loam. Occasional yellowish-brown streaks. Massive to prismatic structure. MnO_2 concretions. Org. C 0·3%; Si/Al 3·30; Si/R 2·55.
C (G)	92+	Bluish-grey heavy loam. Calcareous. Massive to prismatic structure. Occasional brown marblings. Org. C 0·3%; Si/Al 3·32; Si/R 2·60.

The field characters point unmistakably to the influence of groundwater in profile development. The hold-up of downward percolations is not, however, complete, and a rudimentary development of podzolic A and B horizons is suggested by field observation and confirmed by the data for the composition of the clay fraction. It may be noted that the profile is decalcified to about 77 cm. There is about 10 per cent. of calcium carbonate in the raw boulder clay. Mechanical analyses suggest mechanical illuviation with maximum clay, about 34 per cent., at 50–130 cm., as against 20–5 per cent. in the upper horizons and 30 per cent. in the deep boulder clay. It is possible, however, that the lower clay figures in the upper horizons may be due to lateral removal of finer particles. The sharp fall in organic carbon content at 18 cm. marks the limitation of root development by wetness. No figures are given for pH, as this was indeterminable by the quinhydrone electrode owing to the presence of manganese dioxide.

Cryptopodzolic Soils

On account of the general prevalence of grass husbandry in Wales, greyness in the A horizon is often masked by the high proportions of organic matter present. Destruction of humus by hydrogen peroxide treatment will reveal masked bleaching. Masked podzols, the cryptopodzols of C. C. Nikiforoff [2], are found principally among agricultural lands; but one may also find them in small areas of semi-open scrub-oak (*Quercetum petraeae*) woodland with gramineous ground vegetation. Such areas represent the remains of the primitive forest vegetation of the region. They have survived only because of their unsuitability, through rockiness or steepness, for agricultural use.

An example of a cryptopodzolic soil is Profile VIII, from Mynytho, west Caernarvonshire. It occurs at about 70 metres on sloping ground with free drainage. The mean annual rainfall is about 1,000 mm. The parent material is weathered acid igneous rock (porphyritic rhyolite). The vegetation is old grassland, tending to acidic grassland. The data are as follows:

Horizon	*Depth (cm.)*	*Description*
A_{0-1}	0–20	Dark greyish-brown moderately stony, light loam. Org. C 3·55%; pH 5·5; Si/Al 2·57; Si/R 1·93.
B_2	20–31	Bright yellowish-brown moderately stony light loam. Org. C 1·4%; pH 5·3; Si/Al 2·16; Si/R 1·62.
B_3	31–46	Pale slightly greyish yellowish-brown moderately stony light loam. Org. C 0·5%; pH 5·4; Si/Al 2·17; Si/R 1·72.
B_4 (C)	46+	As above, but more stony, passing to rock brash. Org. C 0·2%; pH 5·5; Si/Al 2·67; Si/R 2·09.

The figures for the clay fraction show clearly the B character of the second and third horizons.

Cryptopodzols are of common occurrence in Wales. They are probably analogous to certain soils, occurring in north-west Spain and Portugal, described as *acid humic soils* by E. H. Del Villar [1].

Truncated Podzols

These soils are of widespread occurrence in north Wales, particularly in regions with strong surface relief. They are distinguished by the sesquioxidic character of their surface horizons. This is generally shown in the field by warm brown colours which, however, may be partially masked by organic matter. When the humus is destroyed by peroxide treatment the ferruginous colour is at once evident. The sesquioxidic character of these soils is plainly indicated by the composition of the clay fraction.

It may be presumed that these soils owe their distinctive character to removal of a former A horizon by erosion. This removal may have taken place catastrophically, following destruction of the original vegetative cover, but it is possible that a contributory cause has been normal erosion resulting in the continuous removal of an incipient A horizon [3].

Although catastrophic erosion may have occurred in the past, it scarcely operates at the present day, for these soils are now stabilized under permanent grass or under a rotational system including long periods under grass. And therefore, although the surface horizons of soils of this class show a B character in their clay fractions,* they possess the high organic-matter content and structure of soils that have long been in agricultural production. Some of these soils are indeed of fair productivity. Their main disadvantage is their shallowness and consequent liability to drought. They may also present a problem by phosphate fixation, unless adequately limed.

A typical example of a truncated podzol is seen in Profile IX at Plas Gwyn, Four Crosses, Caernarvonshire. It occurs on a gentle slope at about 60 metres. At the time of sampling the field was oat stubble, part of a short arable break in a rotation mainly grass. The profile is developed in shallow glacial drift of rhyolitic (acid igneous) material.

Horizon	*Depth* (*cm.*)	*Description*
I	0–28	Dark brown slightly stony loam. Org. C 4·1%; pH 5·0; Si/Al 2·20; Si/R 1·68.
II	28–44	Yellowish-brown pebbly loam. Org. C 1·65%; pH 1·65; Si/Al 1·94; Si/R 1·54.
III	44–69	Pale yellowish-brown gritty and brashy light loam, passing to brash. Org. C 0·4%; pH 5·0; Si/Al 2·47; Si/R 2·01.

The B character of the first two horizons is strongly marked by the composition of the clay fraction, and the colour sequence, particularly on the peroxided samples, also strongly suggests succession from B, in the first two, to C in the third horizon.

* The sesquioxidic character of the clays is probably a contributory cause of their structural stability.

Even more extreme instances of truncation may be found in the mountain regions. In one case the mineral horizon below the surface was found to have a clay SiO_2/R_2O_3 ratio of 0·73.

Whilst truncated podzols are generally rather shallow, deeper profiles may occur in regions of moderately flat topography. These form transitions to brown earths as the B character of the upper horizons becomes less pronounced. The moderately deep soils developed in glacial sands of Triassic and Carboniferous origin generally fall into this sequence.

In upland regions shallow truncated soils with sesquioxidic horizons are generally occupied by acidic grassland (*Agrostis* spp. and *Pteridium aquilinum*) vegetation. This community, particularly at its upper altitudinal limit, tends to degenerate to heath with *Calluna vulgaris* or *Erica cinerea* and *Vaccinium myrtillus*. The change is accompanied by the development of a bleached A_2 horizon under raw humus. This development becomes more pronounced in passing away from the boundary of the *Pteridium–Agrostis* community. Such podzolic profiles must be regarded as secondary in character, consequent on a truncated podzol phase.

Brown Earths

The surviving natural forest in Wales is restricted to small areas which, owing to the steepness or broken topography, have not been brought into agricultural use. In such areas profile development is necessarily rudimentary and shallow cryptopodzolic soils are the general rule. Most of the agricultural soils with natural free drainage and fairly level topography may be described as agricultural brown earths. Bearing in mind the predominance of grassland in Welsh agriculture and the fact that even where arable cultivation is practised it forms only a short break in a mainly grass rotation, the qualification 'agricultural' applied to Welsh brown earths carries a special significance. Indeed, it might almost be permissible to describe them as grassland brown earths.

These soils resemble the deeper truncated podzols described above and are connected with them by an unbroken transition. They are distinguished from them by their less markedly sesquioxidic character, and by the general uniformity in composition of the clay fraction down to and including the parent material. In distinguishing these soils from the deeper truncated podzols use may be made of the clay-fraction data. In the latter class the C horizon where reached is shown by a sharp increase in the silica–sesquioxide ratio from less than 2·0 to 2·0 or more. In the brown earths this sharp increase is not observed and the ratio, in soils of primary weathering, approximates to 2·0. It may be presumed, however, that some removal of A material has taken place in all cases, for the Si/R ratio is generally less than 2·0 in the upper horizons.

An example of a Welsh agricultural brown earth is given by Profile X from Ynys, Caernarvonshire. It occurs under grassland on a slight slope at about 60 metres under a mean annual rainfall of about 1,150 mm. The parent material is boulder clay of mixed origin, mainly from acid igneous rocks and hard shales and grits.

The following are the field characters:

Horizon	*Depth (cm.)*	*Description*
I	0–18	Dark brown stony light loam. Org. C 7·0%; pH 5·5; Si/Al 2·55; Si/R 1·97.
II	23–46	Sharp transitions to bright yellowish-brown very stony light loam. Org. C 1·2%; pH 5·2; Si/Al 2·42; Si/R 1·92.
III	46+	Gradual transition to brownish- or yellowish-grey very stony light loam (boulder clay). Org. C 0·6%; pH 5·4; Si/Al 2·63; Si/R 2·07.

The figures indicate a very uniform type of clay fraction and the absence of any marked eluviation or truncation. A profile such as the one just described marks the one end of a gradation of which the other end is a truncated podzol such as the Plas Gwyn profiles. More commonly, intermediate stages are encountered; these may be exemplified by Profile XI from Bryn, near Caernarvon. It occurs at about 60 metres with gently sloping topography. The mean annual rainfall is about 1,050 mm. and the parent material boulder clay, mainly composed of acid igneous debris. The vegetation is old grassland. The field description is as follows:

Horizon	*Depth (cm.)*	*Description*
I	0–33	Dark greyish-brown pebbly light loam. Org. C 4·6–2·7%; pH 4·7–4·8; Si/Al 2·46–2·32; Si/R 1·89–1·78.
II	33–56	Yellowish-brown, passing to colder greyish-brown stony light loam. Org. C 1·0%; pH 5·2; Si/Al 2·22; Si/R 1·72. Transition to—
III	64+	Raw rubbly pale grey stony boulder clay. Org. C 0·3%; Si/Al 2·56; Si/R 2·03.

General Discussion

The soils described in the present paper show the effect of parent material and soil-forming factors, including human interference, on profile characters. The soils of Wales, although developed from ancient rocks, are themselves relatively juvenile and skeletal. This is due partly to the comparatively short time that has elapsed since the last glaciation and partly to the generally strong surface relief, which opposes maturity of development. There is generally little evidence of mechanical illuviation. Whereas in the deeper profiles some increase in the clay content is observable in the B horizon, most of the shallower profiles show an actual decrease in clay content in passing from the surface horizons downwards. Nevertheless, differentiation into horizons as a result of chemical eluviation is evident, even in skeletal soils.

Wales is predominantly a region of podzolic soils, a circumstance that might be expected from the very humid climate. The occurrence of podzolic soils, however, even where maturity of development is attained, must represent a balance between the podzolizing tendency implied by the humid climate and the resistance to podzolization of the parent material. And, therefore, it is not possible to define a podzolic

region in terms of climate alone. Even in a rigorous climate such as that of Iceland, according to F. Weis [4], podzolic soils are not developed in basic parent materials. On the other hand, where parent materials are excessively poor in basic constituents as in highly quartzose sands, podzols may be expected, and do actually occur even in comparatively dry climates.*

Most of the soil of Wales has been modified by human interference, and it is not easy to decide to what extent the original profile characters have survived. It is certain, however, that they have been modified in two respects. In the first place, it seems probable that when the country was first deforested considerable erosion took place. Owing to the smaller intensity of the rainfall this was not on a scale comparable with that in the forest region of the south-east United States, but it must have been sufficient to result in a marked truncation of upland soils and a deposition of eroded material in valleys and hollows, now generally characterized by impeded drainage and, in many localities, peat formation. In the second place, as a result of deforestation and subsequent utilization for grazing or grassland agriculture the country became largely covered with a gramineous type of vegetation, some of which was of an acidic grassland type passing to heath, whilst in areas of impeded drainage, moorland and bog types associated with peat formation were established. In this connexion it may be noted that deforestation itself may result in swamping, owing to the smaller moisture requirements of the vegetation succeeding forest. Apart from this, dry heath types may become wet owing to impedance through the development of impervious B horizons, as in Profiles IV, V, and VI. Much of the present upland peat appears to have succeeded an earlier podzolic stage under heath vegetation.

Where land has been under the typical Welsh grassland husbandry, with periodic arable breaks, the podzolizing processes are arrested, partly owing to the maintenance of a relatively high lime status and partly owing to the prevention of raw-humus development. During recent generations, however, there has been a considerable neglect of liming, and land left for long periods under a poor grass cover is probably undergoing podzolization. This is suggested by the appearance of such species as *Calluna vulgaris*, *Erica cinerea*, and *Vaccinium myrtillus* in the herbage, and incipient greying of the horizon immediately below the turf mat, which develops into a raw-humus layer.

As may be expected in such a humid climate, and with the prevalence of non-calcareous parent materials, the base status of Welsh soils is naturally low. Exchangeable bases, however, are always present even in the soils of waste lands. This may be attributed to the presence of weatherable minerals in the parent materials. The actual base status of a soil represents a dynamic equilibrium between liberation of bases by weathering and removal by leaching, grazing animals, and cropping. It may be conjectured that the change from deciduous forest to grassland

* The best-developed podzols in Britain actually occur in southern and south-eastern England in a relatively dry climate. There the parent materials are highly quartzose Tertiary sands, e.g. in the Bagshot area of Surrey and in the New Forest of Hampshire.

was at first accompanied by a fall in base status, for under forest there is a circulation of plant food between the tree and the soil. When grazing or agriculture is practised, a constant impoverishment by crops and stock occurs, only partially offset by return in the form of manure produced on the farm. In the absence of artificial additions it may be expected that equilibrium would be established at a new and lower base status. During recent years there has probably been a fall in the base status of upland soils owing to the more rapid turnover of sheep flocks with the result that considerably larger annual amounts of calcium, phosphorus, and other mineral constituents are lost. The establishment of heath vegetation at the expense of grassland may be a symptom of this deterioration. Fall in base status naturally favours podzolization.

In the light of our knowledge of contemporary soils, vegetation, and agriculture it may be possible to make a tentative reconstruction of the history of soils in Wales.

In the ages preceding historic time, i.e. before the Roman occupation, settlement by man was sparse and shifting in character. Most of the country up to about 500 metres was covered with deciduous forest or swamp. The associated soils, in areas of free drainage, would vary from brown earths to slightly podzolized soils. With impeded drainage, the range would be from gley soils to peat. The extent of peat and impeded-drainage types generally was probably much less than at the present day.

Above the tree limit the vegetation was heath in the drier and moorland in the wetter situations. With these were respectively associated podzolic and gley, peat-podzol, or peat soils. The highest mountain regions were mainly alpine soils or bare rock.

From the time of the Roman occupation onwards deforestation proceeded at an increasing pace. The presence of grazing animals and the practice of agriculture prevented natural regeneration of forest and encouraged the establishment of grassland or heath. The former forest land lying above the limit of agricultural utilization is now occupied almost entirely by gramineous vegetation, apart from certain areas of heath on lighter soils. The agricultural soils are also largely under grass, either permanent pasture or long-term grass leys.

The prevalence of a grass vegetation has strongly affected the general character of the soil profiles. The principal effect is on the organic-matter status, which is generally high, and probably markedly above that of the preceding forest soils. Even in visibly podzolic profiles, relatively high proportions of organic matter are found in the A_2 and B horizons. The A_2 horizon is often masked by organic matter and can be detected in the field only by a slight greyness and the bleaching of quartz grains. The high organic-matter status is also responsible for a more granular or crumb-like structure in the A horizon than is generally found in podzols.

In the period following the original deforestation and preceding the general establishment of a grass vegetation, it may be presumed that considerable erosion took place. This resulted in a truncation of large areas of podzolized or slightly podzolized soil. As a consequence, much of the grassland at higher levels in regions of convex relief has been

established on former B horizons. In some cases these are undergoing secondary podzolization as heath vegetation extends itself. The material, predominantly of A character, removed by erosion was partly transported into rivers and lost to the land, but it may be supposed that there was also a considerable accumulation in regions of concave relief. At the present day such areas are largely occupied by greyish stoneless soils with impeded drainage. In extreme cases peat soils have developed.

At the present day erosion is inappreciable and is certainly not a major agricultural problem. This satisfactory position is due partly to the general absence of intense downpours, but above all to the good structure imparted to the soil itself by its grassland character. Even soils under arable cultivation are rarely more than 3 years out of grassland; such soils even on steep slopes and with moderately intense downpours are quite stable. The sesquioxide character of the clay in many of our soils would also favour structural stability.

Briefly, Wales may be described as a region of podzolic and gley soils, in which, however, the original characters have been considerably modified by human interference. The most important effect of this interference has been the substitution of grass for forest vegetation. This has led to a general raising of the organic-matter status and an improvement in structure in comparison with the primitive soils of the country. At the same time, owing to the accumulation of downwash in hollows there has probably been a considerable increase in the area of gley soils and peat.

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UNDERWATER 'SOILS': A REVIEW OF LAKE SEDIMENTS

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Introduction

The title is designed to emphasize that underwater sediments may be regarded as soils of a special type. Widely varied as they are, sediments differ from most sub-aerial soils in two important respects. Firstly, they are generated more or less continuously by sedimentation from above and are normally left undisturbed. Secondly, they are permanently waterlogged, a gas phase being absent except for the methane which is sometimes formed under anaerobic conditions. One important feature of the sedimentation process is the sorting of the particles by size according to the degree of movement in the water above. A wide range of variability in particle size, as well as in parent material (inorganic and organic), yields a bewildering variety of types which can only be described or classified in general terms. Not only may great variation be expected from lake to lake, but also in different regions and in different epochs in any one lake. Furthermore, the surface is continually being buried by fresh material. Progressive changes, such as consolidation and decomposition of all but the more resistant organic matter, yield a sediment which changes in character with age and depth.

Therefore, in order to avoid becoming lost in descriptive detail, this article will deal with the general features not only of the sediments themselves but also of the processes in the water above them and the conditions in the lake drainage basin.

Range of Sediment Studies

Studies of sedimentation and sediments have been pursued for a variety of reasons: navigation; engineering; geology; geochemistry; history of climate and vegetation; physics, chemistry, and biology of natural waters. Brief references can only be made here to general reviews of some of these aspects.

Although navigators have always recognized qualitative differences in the sea-bed, it was the demands of cable engineers, among others, for better knowledge of conditions in the oceans and on the ocean bottom that led to the expedition of H.M.S. *Challenger* 1873–6 specifically equipped to study these conditions [1]. In turn, the *Challenger* material, supplemented later by other expeditions, proved an important source of geochemical data [2]. Sedimentary geology, too, is logically approached through a study of modern sediments. Recent views that the origin of petroleum is to be found in microbiological activities in marine sediments [3] have focused attention on sediment investigations; cf. numerous papers in *J. Sedimentary Petrology* and the very useful symposium [4] published by the American Society of Petroleum Geologists.

A considerable body of Swedish work on the regional distribution of lake-bottom deposits [5, 6] received its stimulus from H. von Post's early work on peat [7].

Two further useful general reviews may be noted [8, 9]. Some references to particular investigations centred round the relation of sediments to living plants and animals and to the chemistry of the aquatic environment will be given later.

Sampling Methods

Refinements of sampling technique have an important influence on the precision it is possible to attain in stratigraphic studies. The ideal, not always achieved, is to obtain a complete and undistorted core of deposit from the unconsolidated, often semi-liquid surface to a depth which depends on one's purpose, and which may include many metres of deposit if it is desired to pursue investigations down to the original solid lake bed. In the oceans this operation has to be carried out a mile or two below the ship. Technique has therefore had to evolve considerably since the navigator's ancient device of a piece of tallow on the sounding lead; it has done so along two main lines—grabs and coring-tubes—designed for different purposes [10]. Grabs vary from simple 'snappers' and drag buckets, developed for rapid superficial sampling of large regions, to instruments which take a sample of fixed area and thickness. In some of the more elaborate types it is possible to divide the sample into depth layers for quantitative faunistic studies [11]. Coring-tubes are designed for stratigraphic work on deeper sections of deposit. They are usually simple tubes, with or without core-retaining devices, driven into the deposit by various means including dead weight, momentum [12], explosives [10], and suction. Internal friction invariably leads to compaction of the core; corrections have been attempted [13], but cannot be considered satisfactory. A probable exception is Kullenberg's 'piston' sampler, which has recently taken cores up to 50 ft. in length from the bed of the Atlantic [14]. In this apparatus the weighted coring-tube slides into the deposit over a piston held stationary at the sediment surface, thus tending to create a vacuum below the piston which overcomes internal friction and forces the sediment into the tube. A trap mechanism at the mouth of the tube prevents the core from escaping.

Another solution of the compaction problem is to take short overlapping cores [35] or to separate the driving and core-cutting operations. In Reissinger's modification of the Hiller peat-borer [15] and in the Jenkin core-sampler [16] the apparatus is first driven to the required depth; core-cutting then takes place radially into undisturbed deposit. Accurate stratigraphic results can be obtained in this way, but a well-anchored platform is necessary and the complete core must be reconstructed from a set of overlapping samples.

Factors which influence Sedimentation

Leaving aside those factors related to the origin of lakes [9], we may recognize three interrelated groups which begin to operate as soon as a lake comes into being. These are, firstly, lake properties—area, depth,

shape, production of living matter; secondly, geological and erosion conditions in the drainage basin—type of rocks and soils, vegetation cover, cultivation, pollution; thirdly, climate—rainfall and run-off, rate of rock weathering, wave action, and water movement.

Although the interaction of all these factors is necessarily complex, their influence on the sediments is none the less profound. Increase in lake area means greater wind fetch and more violent erosive wave action on exposed shores; here no sediment can settle. Loose material is automatically sorted according to size and deposited in deeper water in order of decreasing particle size with increasing depth. Again, other things being equal, a longer fetch allows waves of longer length to develop. As wave disturbance decreases exponentially with depth—falling to roughly one-twentieth of the surface value at a depth equal to half the wavelength—increase of fetch extends the depth range of wave action. The gradation of deposits off shore, and from eroded shorelines into more sheltered regions, forms a varied substratum for a succession of rooted plants. These in their turn modify wave erosion and contribute organic material to the sediments. The finest fractions of all, irrespective of source (organic or inorganic, shore erosion, inflow or planktonic growth in the open water) are carried out by water currents and can only settle in deep regions in relatively still water, where they form a more or less uniform mud, characteristic of the lake and its drainage basin. Insufficient light penetrates to these depths for rooted plants to grow.

In shallow lakes, or in those with large areas of shallow water adjacent to the shores, conditions can be very different. Reed-beds and other rooted vegetation absorb wave energy, protect the shores, and yield large crops of organic matter each year. In the absence of mineral silt, decomposition is slow, and peat-like deposits encroach from the shore outwards and may finally fill the lake. Deep lakes, by contrast, fill up with mud from the middle, but far more slowly [17].

If, as is usually the case, the drainage area is large compared with the lake area, then most of the sediment parent material may be expected from the inflows. Drainage slopes, the nature of the rock and its weathering products, extent of soil cover, cultivation, pollution, rainfall distribution, and incidence of floods, all contribute to regulate quality and quantity. It is therefore not surprising that sediments often record changes in these factors [18], sometimes in great detail [19]. The importance of floods should not be neglected. It is probable that more solids are brought in during a few hours of flood, when turbulent rivers can carry a large suspended load, than during all the intervening weeks of low water, when dissolved matter forms the main contribution. The original lake shore becomes progressively modified by the growth of deltas, around which is another depth gradation of particle size with distance from the river mouth. The continuous supply of mineral silt at this point often exercises a profound influence on the distribution of rooted vegetation [20], possibly through its effect on the base-exchange status and decomposition of organic matter in the substratum.

We have briefly considered shore phenomena and conditions in the drainage basin. In very large lakes or in the oceans these become of

secondary importance when compared to the contribution of the plankton. The bottom receives a continuous rain of corpses of these usually microscopic plants and animals; their indestructible parts become incorporated in the bottom oozes.

The Role of Sediments in Lake 'Metabolism'

In common with many other problems in nature, sediments can be studied along two distinct lines. The one—for want of a better word we may call it 'taxonomic'—aims at detailed description and classification of types on a basis of particle size, chemical characters, and organic remains. Attempts to recognize such types and describe their regional distribution have introduced a detailed terminology, mainly Swedish [5, 6, 8]. But in practice the complexity of the parent material and of conditions during and after sedimentation makes any such system seem limited and artificial. In contrast to soils chemical analysis seems rarely to have been the basis for classification [21, 22, 23]. This is surprising, for a large range of mineral constitution, organic content, base-exchange status, &c., exists. In calcareous districts, for instance, calcium carbonate is often precipitated by the activities of plants and bacteria and accumulates in the deposits; in non-calcareous regions a base-poor, acid sediment may result, or sometimes iron and manganese may accumulate. The organic residues also vary from undecomposed peaty remains to well-decomposed humus, depending on such factors as the presence or absence of dissolved oxygen or bases during decomposition.

The other ('metabolic') approach considers the part the sediments play in biological productivity in the lake as a whole, especially their influence on the supply of plant nutrients. It takes a unit volume, either a whole lake or a column of water plus sediment of unit area in the central deep region of a lake, and studies the transfer of energy and matter across its boundaries. It is a convenient approximation, although not always an accurate one, to consider the water-plus-sediment column as a closed system and to neglect gains and losses due to lake inflows and outflow. If this is done, the supply of energy and dissolved oxygen from above and of nutrient salts from below results in gradients along the vertical axis.

Let us first consider processes in the water. In winter, when ice-free, lakes are kept well mixed by wind; the temperature is the same and the water is saturated with oxygen from top to bottom. In spring and summer solar heating decreases the density of surface water, and wind energy is now absorbed in mixing this with colder, denser layers below. The thickness of this superficial, mixed layer (*epilimnion*) varies with dimensions of the lake, weather, and season; in temperate lakes it is of the order 10 to 20 metres. A sharp temperature gradient (*thermocline*) separates the epilimnion from the underlying cold layer—the *hypolimnion*. As we descend into this, the temperature becomes more nearly uniform and, in deep lakes, approximates to that of the whole lake at the time when thermal stratification commenced. The fact that little of the summer heat reaches the bottom shows that the hypolimnion becomes

practically isolated from the epilimnion and therefore from the atmosphere.

This isolation has three important results. Firstly, planktonic algae can usually only find sufficient light for photosynthesis in the epilimnion. Once they have depleted some essential nutrient substance there, they cannot obtain replacements from the hypolimnion. Thus lakes often show a spring outburst of algal growth which comes to a sudden conclusion. Secondly, water movement in the hypolimnion is much cut down. Thirdly, dead organic matter is continually sinking through the thermocline into the hypolimnion, its quantity depending on productivity in the epilimnion. Much of this 'crop' becomes incorporated in the sediments. Its decomposition, plus respiration of animals, bacteria, &c., creates an oxygen demand which can only be met from the store of oxygen trapped in the hypolimnion at the onset of thermal stratification. Here the depth of the hypolimnion exerts an important influence, which will be evident if we compare two lakes of equal productivity, but of differing depth. In both lakes the amount of organic matter sinking through unit area of the hypolimnion surface is the same, as is also the total quantity of oxygen required to oxidize it. The removal of this oxygen from the large hypolimnion of a deep lake will make only a small change in oxygen concentration, whereas in the shallow lake the oxygen may be completely removed from the hypolimnion by the end of the summer. While oxygen depletion proceeds, dissolved salts and CO_2 accumulate in the hypolimnion and, if the oxygen disappears, products of reduction (ferrous iron, hydrogen sulphide, methane, &c.) accumulate as well [24].

Autumn cooling and autumn gales combine to increase the thickness of the epilimnion until the whole lake becomes completely mixed again at the *overturn*. Atmospheric oxygen is then again carried down to the deposit surface.

At the surface of a deep lake mud these seasonal changes are experienced as fluctuations in the rate of delivery by turbulent water movements of oxygen to the mud surface. Meanwhile, as we have seen, organic matter (dead plankton) is continually sinking to the bottom and its decomposition creates an oxygen demand. Neglecting disturbances due to bottom-living animals, oxygen can only enter the mud by molecular diffusion, and it is usual to find that it is all used up at levels more than a few millimetres below the mud surface. This boundary between the free-oxygen layer and the lower anaerobic layer is an important one in the mud–water column. Its position represents a dynamic balance between rates of oxygen supply and consumption [24]. As we have seen, in shallow lakes in summer, if the rate of oxygen supply to the mud surface falls too low, this boundary rises into the water and comes to lie at the thermocline.

An advance in sampling technique [24] has enabled undisturbed samples of the upper 10–20 cm. of the mud, together with 40 cm. of the overlying water column, to be collected in order to follow in detail seasonal fluctuations in the oxidation–reduction boundary in some lakes in the English Lake District. This was conveniently done by measuring

potentials, taken to be redox potentials, developed on micro-electrodes of bright platinum, immersed at millimetre-depth intervals above and below the water–mud interface. As had already been noted in water-logged soils [25], these potentials agreed closely with chemical evidence of oxidation or reduction. Indeed it was found possible to assign a definite potential level (0·2 volt at pH 7·0) to the boundary between oxidized and reduced phases. At this boundary potential were found: ammonia but no nitrate, an oxygen concentration of less than 1 mg./l., Mn^{++}, traces of Fe^{++}, sulphate partially reduced to sulphide. Potentials above and below this value showed corresponding shifts of chemical balance in oxidized or reduced directions. The potential measurement gives, therefore, a useful indication of the oxidized or reduced state of the system in conditions, e.g. within the mud, under which chemical determinations would be difficult.

Fig. 1 illustrates seasonal changes in Esthwaite Water. Oxygen concentration in the water column was initially high and uniform. Concentration in the lower layers fell progressively after thermal stratification had set in during the middle of May. The corresponding temperature diagram, omitted here, shows that a thermocline developed at 6 m. depth and fell fairly steadily to 9 m. at the end of August, then more rapidly as the overturn approached. The oxygen gradient during August and September was at thermocline level. Turning to the water–mud interface, we see a corresponding shift of the boundary potential, indicated by a thicker contour, from its winter level at approximately 10 mm. below the mud surface to a summer position in the water. Its rapid rise to the thermocline after 'escaping' from the mud is due to the change-over from molecular diffusion in the mud to (albeit much reduced) turbulent transport operating above the interface. After the return of full aeration of the bottom at the overturn, the system reverted to the winter condition, later modified by ice cover.

In deeper lakes, in which oxygen at the bottom was not completely exhausted, the upward summer shift of the boundary level was confined within the mud.

Although detailed description of the reduction process must be omitted, one remarkable feature should be noted. Reduction was accompanied by the appearance in the water of large quantities of some dissolved substances (lower portion of Fig. 1). Some of these, Fe^{++}, NH_4^+, and others not shown (Mn^{++}, S^{--}, soluble organic compounds) could be regarded as products of reduction. But others, silicate, phosphate, NH_4^+ not accounted for by nitrate reduction, bases other than Fe^{++}, &c., could not be so regarded. Although the mechanism involved cannot as yet be described in detail, the behaviour of iron provides the key.

At the pH of most natural waters ferric iron is practically insoluble, and there is evidence that the small amounts actually found are in particulate or complex form [26]. Ferrous iron, however, is soluble and below the boundary potential is free to diffuse, although at lower potentials it may be again precipitated as ferrous sulphide. Any ferrous iron which diffuses up into contact with oxygen in the mud surface is re-oxidized to the insoluble ferric condition and accumulates there, probably

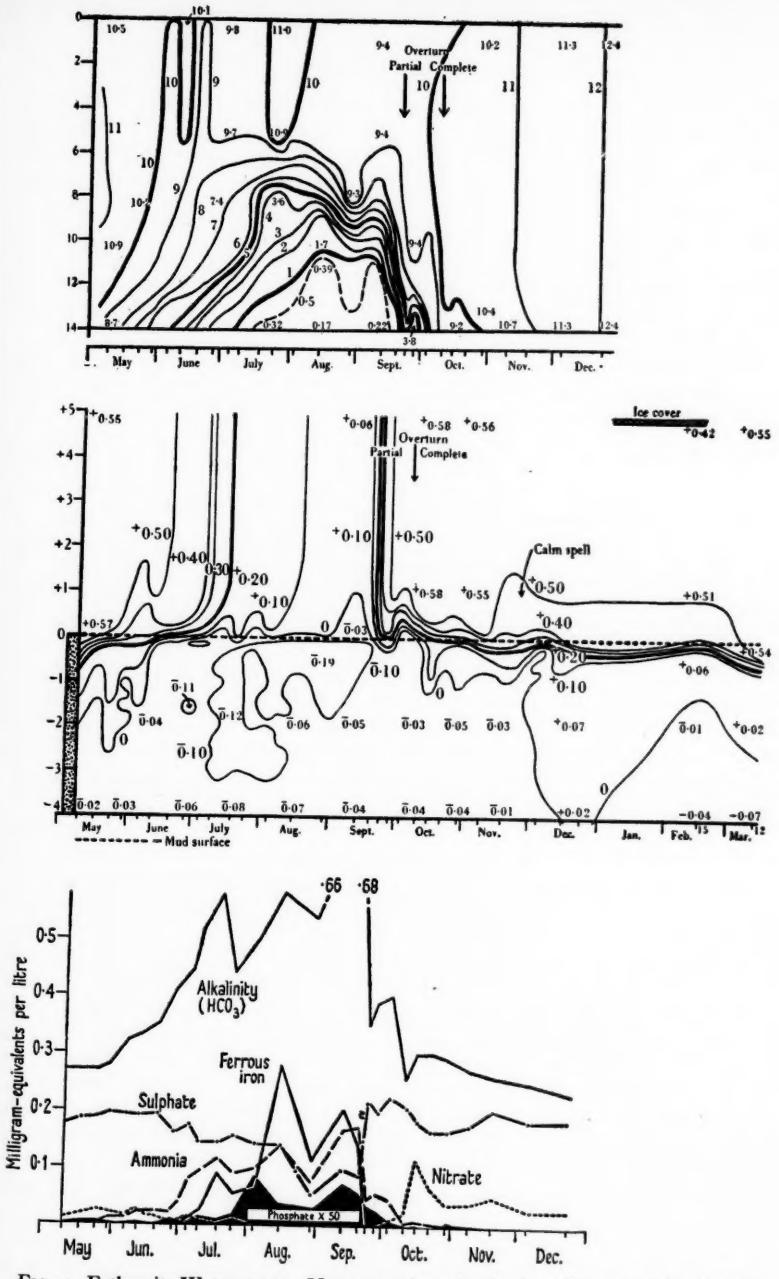

FIG. 1. Esthwaite Water, 1940. Upper portion; depth–time diagram of the distribution of dissolved oxygen (milligrams per litre) in the water. Middle portion: depth–time diagram of the distribution of redox potential (volts adjusted to pH 7·0) above and below the mud surface. Lower portion: concentration (milligram-equivalents per litre) of some dissolved substances in water samples taken approximately 10 cm. above the mud surface. Note: the upper and middle portions are Figs. 27 and 28 (reproduced by permission of the *Journal of Ecology*) and the lower portion is redrawn from Fig. 29 of Ref. No. 24.

mainly as ferric hydroxide. Where sufficient iron is present it gives a distinct brown coloration to the surface few millimetres of the mud. This material is flocculent and forms a strongly adsorbent blanket blocking free exchange of ions between the lower mud and the water. The adsorbent properties of bottom muds have been known for some time in the practice of fish-farming. Lime, phosphate, and other fertilizers are added to the ponds usually in one lot in the spring. The fertilizer rapidly disappears from the water and, although water is continually flowing through the pond, the effect of manuring can be observed for several years [27].

If, but only if, this surface ferric floc is destroyed by reduction during the summer, adsorbed substances are liberated, insoluble ferric phosphate is reduced, and diffusion between mud and water can continue unimpeded.

Activities of Bacteria and Animals in Sediments

Little more than exploratory work has been done on the microbiology of sediments [3, 28, 29]. It is known that numbers of bacteria are very large compared with those found in the water. Decomposition of organic matter and the attendant oxygen demand are the result of microbiological activity. Organic residues, as in soil, are of a humic nature [7]. ZoBell [30] recognizes three types of oxygen demand in marine sediments: firstly, chemical absorption after bacteria and enzymes have been destroyed by mercuric chloride; secondly, slow, enzymatic absorption after sterilization with toluol or chloroform only; thirdly, respiratory absorption which is initially low and increases to a maximum as bacteria multiply.

ZoBell also distinguishes between reducing *intensity* (e.g. measured by redox potential) and reducing *capacity* (rate of oxygen uptake). Although reducing intensity may often increase with increasing depth in the sediment, it is usual to find that reducing capacity is highest in the surface. At the mud surface he found several million bacteria per gm. of wet mud (plate counts) with aerobes predominant, while there was less than 10 per ml. in the water a few metres above. But numbers fell rapidly with depth in the mud; anaerobes predominated at lower levels; viable bacteria were still found at considerable depths in cores. As in soils, bacteria showing a wide range of biochemical activity have been isolated from lake water [31] and marine muds [3].

The activities of animals in the deposits are often overlooked. Many invertebrate groups are represented, with insect larvae, mollusca, and oligochaete worms quantitatively predominant. Variety of species is greatest in the littoral zone; fewer species inhabit deep muds, although numbers may be large. Insect life-cycles impose large seasonal fluctuations in quantity; extensive migrations occur. The bulk of the organisms is found in the top 15 cm. of the deposit; a few are found as deep as 30 cm. [11]. Like earthworms, their feeding activities result in a thorough 'working' of the sediment, help to break down organic matter, and account for the absence of stratification in many deposits [32].

Only a few specialized species (e.g. some Chironomid larvae and *Tubifex*) can adapt themselves to the low oxygen content prevalent at the mud surface in some shallow lakes in summer. They survive by means of various devices; building tubes to raise themselves into better oxygenated water, possession of special respiratory pigments, capacity to run up large physiological 'oxygen debts' which are paid off when oxygen returns [11, 33].

The distribution of species, numbers, and weights with water depth is closely related to plant cover, particle size, and organic content of the deposit and to oxygen conditions in the hypolimnion. As with plankton production, high productivity is generally only found in shallow lakes. The reasons for this are complex and not fully understood. A summary of data for lakes in various parts of the world [33] shows that in lakes of more than 25 m. mean depth the total 'crop' was never higher than 400 kg./ha., whereas in shallower ones weights of up to 1,800 kg./ha. (including molluscs) have been recorded [11].

These bottom organisms form part of the food of fish. In comparing the 'useful' annual protein production of soils and natural waters, it is worth noting that properly designed and treated fishponds can produce, often on very poor land, protein crops in excess of beef production on the best pasture [27].

Questions for the Future

The organic cycles in the soil, in the sea, and in fresh water have many features in common. In all three media we find productivity regulated by the rate of supply of energy and nutrients. Thus, findings in soil science have a direct bearing on problems in oceanography and limnology. In conclusion, therefore, it may be in the interests of closer co-operation to indicate some important questions, relating to the central problem of biological productivity in the water-sediment system, to which no answer or only a partial one can be given.

For instance, it is a matter of observation that high productivity per unit area in lakes is associated with either shallow depth or a base-rich medium or, more often, with both. Precise reasons for this are difficult to adduce. Is it because the planktonic algae spend more of their life span in the light than in a deep lake, or because more nutrients may be liberated from the sediments during reduction of the hypolimnion in summer, or simply the observed fact that shallow and silted lakes are almost invariably associated with drainage valleys well covered with cultivable soil [34], or a combination of some or all of these factors? In general, a lake situated in a rich agricultural area is highly productive, and this is not surprising if the lake inflow is regarded as soil leachate. Further, what is the precise role of bases, notably calcium, in raising the concentration level of other nutrients and markedly increasing productivity, both in the lake water and in rooted vegetation on the marginal sediments?

Turning to the more limited field of oxidation–reduction conditions at the sediment surface, many questions remain. When the surface adsorbent layer becomes reduced, how much of the liberated store of nutrients eventually becomes available to plants in the illuminated

surface waters, and how much becomes re-adsorbed by fresh ferric floc after the overturn? What is the significance of the potentials observed? How far are they poised by reversible redox systems or how far, in view of the fact that the oxidized forms of both iron and manganese are removed from solution, must they simply be regarded as the result of a dynamic balance between the rates of supply of oxygen and reducing ions? In this connexion it will have been noted that the 'boundary potential' lies well below the theoretical potential of a balanced ferric/ferrous system. Finally, it should be of interest to discover how far the various biochemical activities of micro-organisms are located at definite energy levels in the redox gradient.

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THE DEPENDENCE OF TRANSPIRATION ON WEATHER AND SOIL CONDITIONS

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1. *Introduction*

DURING the past few years experiments have been conducted at Rothamsted on the meteorology of evaporation from open-water surfaces, and of transpiration from short grass kept plentifully supplied with water by maintaining a water-table just below the root zone. An account of this work has been published elsewhere [1], but as it forms the basis of the present paper a brief summary is desirable for the sake of completeness. For open water, two theoretical conceptions were used. In the first, evaporation was regarded as due to a vapour-flow produced by a difference in vapour-pressure between the water surface and the air above, the flow-rate being dependent on wind speed. A semi-empirical equation to represent the rate of evaporation was obtained in two forms:

$$E_o = 0{\cdot}35(e_s - e_d)(1 + 9{\cdot}8 \times 10^{-3} u_2) \text{ mm./day}, \quad (1)$$

or

$$E_o = 0{\cdot}37(e_s - e_d)B \text{ mm./day}, \quad (2)$$

where e_s is the mean saturation vapour-pressure at the water surface, determined by the mean surface temperature, T_s;

e_d is the mean vapour-pressure in the air as measured in a standard screen;

u_2 is the wind velocity in miles per day measured at 2 m. above ground-level;

and B is the mean Beaufort force, measured at 10 m. above ground-level.

The second of these equations is less precise, but, as British weather records only report wind speed as a Beaufort force, it is the only possible form for general use.

The second conception was based on the identity of evaporation as an energy change, the process requiring a supply of latent heat of vaporization, and an attempt was made to draw up an energy balance-sheet leaving evaporation as the only unknown. The process was in two stages. In the first, an expression was obtained for the total amount of energy (H) available for evaporation and heating of the air; in the second, the division of this energy between evaporation and heating was decided.

$$H = R_C(1 - r) - \sigma T_a^4(0{\cdot}56 - 0{\cdot}092\sqrt{e_d})(0{\cdot}10 + 0{\cdot}90n/N), \quad (3)$$

or

$$H = R_A(1 - r)(0{\cdot}18 + 0{\cdot}55n/N) - \sigma T_a^4(0{\cdot}56 - 0{\cdot}092\sqrt{e_d})(0{\cdot}10 + 0{\cdot}90n/N); \quad (4)$$

$$E_o = H/(1 + \beta), \quad \text{where} \quad (5)$$

$$\beta = 0{\cdot}27(T_s - T_a)/(e_s - e_d). \quad (6)$$

In these equations the symbols are as follows:

R_C is the short-wave radiation from sun and sky, measured in the equivalent number of millimetres of water that would be evaporated per day if it were all used up in this way;

R_A is the theoretically calculable amount of radiation that would reach the earth in the absence of the atmosphere;

r is the fraction R_C reflected. This will be taken as 0·05 for open water;

σT_a^4 is the theoretical black-body radiation at air temperature, T_a (in evaporation units like R_C and R_A);

n/N is the ratio of actual to possible hours of sunshine. Its appearance in the first term of (4) is an attempt to use sunshine records to estimate total short-wave radiation; it appears in the second term because it is used as a measure of the cloudiness that controls back radiation from the earth to the sky.

In each of the two groups of equations appears either the surface temperature or its derived parameter the surface vapour-pressure. Always difficult to measure, it does not appear in any routine records of weather stations, but a little elementary algebra shows that it can be eliminated by equating the estimates of (2) and (5). If we represent by E_a the value of E_o obtained by putting $e_s = e_a$ in (1) or (2), where e_a is the saturation vapour-pressure at the air temperature,

then,
$$E_a/E_o = (e_a - e_d)/(e_s - e_d)$$
$$= 1 - (e_s - e_a)/(e_s - e_d). \quad (7)$$

Also
$$H/E_o = 1 + 0{\cdot}27(T_s - T_a)/(e_s - e_d),$$

and if we put $(e_s - e_a) = \Delta(T_s - T_a)$, where Δ is the slope of the $e : T$ curve at $T = T_a$, then

$$H/E_o = 1 + 0{\cdot}27[(e_s - e_a)/(e_s - e_d)]/\Delta. \quad (8)$$

From (7) and (8) the vapour-pressures can be eliminated to give

$$E_o = (\Delta H + 0{\cdot}27E_a)/(\Delta + 0{\cdot}27), \quad (9)$$

in which all unknowns are either air parameters or obtainable from standard tables of constants. The weather elements required are mean air temperature, mean air vapour-pressure, mean wind force, and mean duration of sunshine. All, with varying degrees of difficulty, can be abstracted from the *Monthly Weather Report* of the Meteorological Office, to enable retrospective estimates of evaporation-rates to be made for well-exposed surfaces of open water.

For the turf, although attempts are being made to provide an analytical approach, the present knowledge is primarily empirical. As provisional estimates, based on results in 1944 and 1945, the ratios of transpiration from turf (E_T) to evaporation from open water (E_o) similarly exposed are:

	E_T/E_o
Nov.–Feb. (incl.)	0·6
Mar., Apr., Sept., Oct.	0·7
May–Aug. (incl.)	0·8
Year	0·75

These ratios might vary with the latitude of the station, due to the changed distribution of day-length throughout the year, but as they have already been rounded off they should be applicable to most of the British Isles.

The ratios are for conditions in which the grass always has plenty of water available, and the few checks possible on other data showed that they were reasonably reliable. In many years, however, particularly in southern England, natural turf suffers from lack of water, transpiration- and growth-rates are reduced, and the problem of estimating the net deficit of water built up in the soil, while remaining fundamentally meteorological, has biological and soil aspects added to it.

The purpose of the present paper is to outline a possible method of approach to the problem. It is largely speculative, but it may be useful in showing gaps in our knowledge and in indicating how to attempt to fill them.

2. *Soil-moisture Deficits under Pasture with Limited Rainfall*

(*a*) *Root range and available water*

Although many factors may alter it, one can ascribe to herbage a more or less definite root range in the soil, of the order of a foot or so. In this depth of soil there will be, at field capacity, a certain amount of water readily available for the plant upon which it can draw as easily as the turf referred to in the experiments outlined in paragraph 1. As an order of magnitude, the available water might be equivalent to 3 in. of rain, i.e. under the stated conditions the grass would be able to transpire 3 in. of water without needing to draw on supplies below the root zone, and without water-supply limiting the rate of transpiration. This, in effect, is an acceptance of the Veihmeyer [2] concept of available water postulating a very narrow range of moisture content, or more correctly soil suction, on one side of which water is readily available, and on the other side of which the water is not available. The depth of the root zone, and the available water in it, might depend upon the composition of the herbage, its manurial treatment, the nature of the soil, the nature of the crop management, and the rainfall in the early part of the growing season. For the last two, for instance, one would expect frequent cutting to reduce the root range, and would expect a dry spring to increase it. Specification of the 'root reservoir' of water will be almost entirely guess-work, but the guess should not be inconsistent with the natural or imposed condition of the soil and crop.

(*b*) *Depletion of water below the root range*

The plant roots may be regarded as exerting a drying potential. While they are using up the available water around them there will, of course, be some water movement upward from below, but it is convenient to make the slightly artificial assumption that the roots first use up the neighbouring water before the movement from below attains any appreciable magnitude. The drying after the exhaustion of the root reservoir should be the same as if the drying potential were applied to bare soil initially at field capacity, and its progress will then be represented by the drying curve obtained in laboratory experiments [3] which

compared the evaporation-rate from bare soil with that from open water exposed to the same conditions. As this curve was the same for a sandy soil (Woburn) and a clay (Rothamsted), it will be assumed that it can be safely used for a range of soils.

(*c*) *Composite drying curve for saturated and non-saturated conditions*

It is now possible to build up a drying curve to estimate deficits under a wide range of conditions. As abscissa (Fig. 1) we take the potential

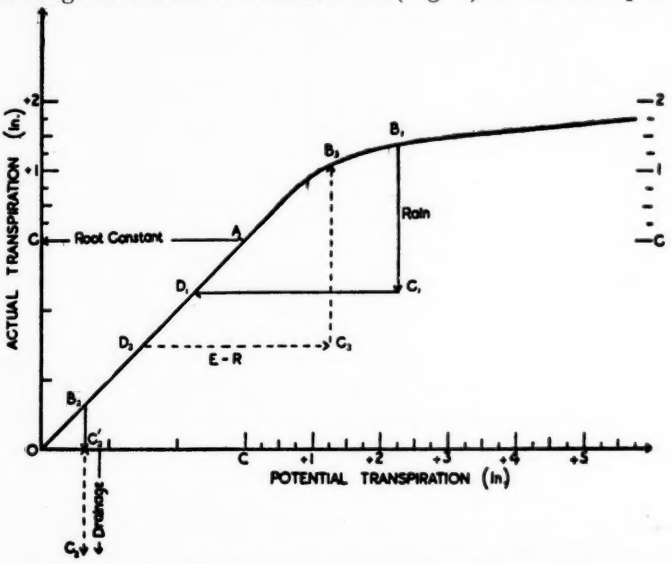

FIG. 1. Composite drying curve for saturated and non-saturated conditions. The particular case illustrated is for a root constant of 3 in.

transpiration, E_T, which will be calculated from weather data. From point A, as a temporary origin, we draw backward a line of unit slope to a point corresponding to the 'root-reservoir' constant on the abscissa. This point is to be the working origin. From A, in the opposite direction we draw the moisture-depletion curve for bare soil. The curve has a slope of unity up to nearly 1 in. and then bends sharply to become, for practical purposes, a straight line of slope of about 1 in 12. When the soil moisture is represented by point O, i.e. at the origin, the soil is at field capacity. As the integrated drying potential increases, the actual drying remains equal to it up to point A (i.e. the root reservoir has been transpired) and slightly beyond it; when it exceeds the root reservoir by more than about 1 in. the actual transpiration-rate decreases rapidly, i.e. the soil-moisture deficit increases very slowly.

(*d*) *The effect of rain*

Rain falling on a soil with an established deficit will raise a layer of definite thickness at the top of the profile to field capacity. If the soil state is represented before the rain by point B_1, after the rain it will be

represented by point D_1, where B_1C_1 represents the amount of rain and C_1D_1 is parallel to the abscissa. If the deficit is smaller than the amount of rain, say, initially at point B_2, then part of the rain (B_2C_2') will be retained to bring the profile up to field capacity and the remainder ($C_2'C_2$) will appear as drainage.

It is assumed that all rain up to an amount equal to the root reservoir will be available for transpiration at maximum rate. This simplifies use of the diagram: for suppose the soil moisture at a given time to be represented by D_3 and that in a given period afterwards the balance of estimated potential transpiration (E_T) over measured rainfall (R) is E_T-R. Adding E_T-R to the abscissa of D_3 brings us to C_3, and the new value of the deficit is given by the corresponding ordinate through C_3: it is represented by the point B_3 on the curve. The treatment may break down if the rainfall is not well distributed over the period: for instance, if it all comes at the beginning of the period and exceeds the initial deficit, then drainage will occur, and the deficit at the end of the period will be underestimated by an amount equal to the drainage.

As an example of the use of the diagram is given in detail below, only one further remark is necessary here. The curve can be made universal by extending section AO indefinitely and using a movable pair of axes on a second piece of graph-paper. [After some experience one can dispense with section AO altogether at the expense of a little more elementary arithmetic, but in the form presented here it gives a better picture of what is happening than the curtailed diagram could do.]

3. *Tests on Other Data*

With a few exceptions to be noted, all the estimates of transpiration potential have been made from data given in the *Monthly Weather Report*. From Table III of the report were obtained the mean air temperature and the ratio of actual/possible hours of sunshine; from Table IV of the report were obtained the vapour-pressure of the air and the frequency distribution of Beaufort wind forces, readily weighted to give a mean value of the wind force. The number of entries in Table IV per station varied: a mean of all available entries has been used.

(*a*) *Cambridge University Farm*

This has been the main testing-ground for the ideas set out in paragraph 2, as it alone has satisfied the condition that there should be contemporary weather data for a site that undergoes drought conditions at times. In one of the clay fields on the farm there is a mole drainage system at 2 ft. below the surface: as it is subject to frequent inspection, there is a complete record of the times of beginning and ending of running of the drains. It is therefore possible to say to within a few days when the field was last at field capacity in the spring, and when it returned to field capacity in the autumn.

The problem can now be stated: given the date of the last spring running, and given the weather data for the following months, can one predict the date of first running of the drains in the autumn? As the month is the unit of time, the prediction may be regarded as successful,

(i) if one predicts the time of running to the nearest week; or, where at a known time of running there is still a predicted deficit, (ii) if the prediction is not greater than about $\frac{1}{2}$ in., i.e. about 1 week's transpiration in midsummer.

The results for the years 1933–9 appear in Fig. 2. In the first trials a root constant of 3 in. was used in all years and was reasonably successful,

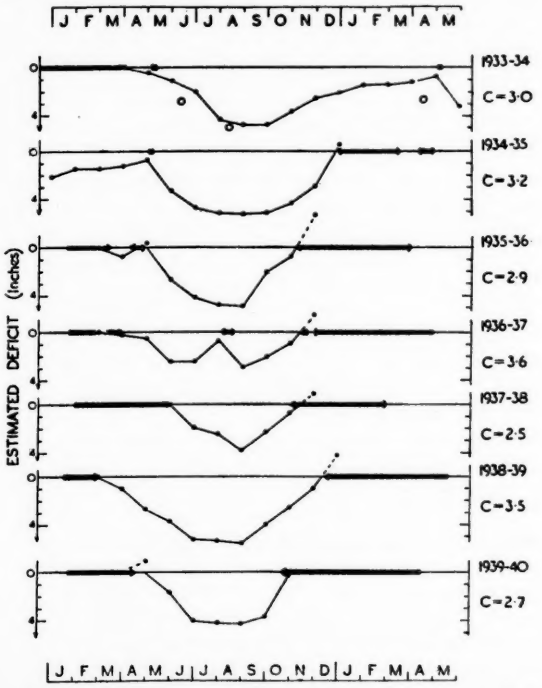

FIG. 2. Seasonal change of estimated deficit at Cambridge. Periods when the field drains were running are shown by thick horizontal lines: the estimated deficit at the end of each month is shown by a full point. A correct prediction of deficit should show it returning to zero at the same time as the drains begin running. Open circles, 1933–4, show values of the deficit as measured by sampling.

but it was noted that an improvement could be effected by increasing the root constant in years with a dry spring, and decreasing it in years with a wet spring. Qualitatively, this is acceptable: indeed, one might impose it *a priori* as a necessary condition to be satisfied, but quantitatively there is no justification other than expediency for the form adopted:

$$C = 5{\cdot}0 - 0{\cdot}6 \sum R, \qquad (10)$$

where C is the root constant in inches and $\sum R$ is the sum of the April and May rainfalls.

It will be convenient to consider the data for 1935 first. The root constant was effectively 3 in. For March the value of $E_T - R$ was

0·67 in.: the drains were not running at the end of March. For April the value of $E_T - R$ was −1·06 in., giving a net estimated deficit by the end of the month of −0·39 in., i.e. the drains should have run in April: they did. Assuming the soil at field capacity on 1 May, the value of $E_T - R$ for May was 2·58 in.: this, being less than C, is also the deficit expected at the end of May. For June, $E_T - R$ was 1·58 in.: added to the existing deficit of 2·58 this brings us to the bend in the curve and the actual net transpiration for June is estimated at 1·50 in., giving a total deficit of 4·08 in. at the end of June. For July, $E_T - R$ was 3·42 in.; according to the curve, only 0·60 in. of this could be transpired, and the deficit therefore increased to 4·68 in. by the end of the month. For August, $E_T - R$ was 1·38 in.; from the curve, 0·12 in. would be transpired, giving an end-of-August deficit of 4·80 in. For September, $E_T - R$ was −2·76 in.; the deficit was, therefore, reduced by this amount to 2·04 in. For October, $E_T - R$ was −1·38 in., and the deficit was reduced to 0·66 in. For November, $E_T - R$ was −3·35 in., giving a 'deficit' of −2·69 in. by the end of the month, that is, the drains should have run during November, probably early in the month. The drains did run as predicted.

Predictions for 1937 and 1938 were equally successful, using (10) for estimating C. [A change in C of 1 in. increases the maximum deficit by slightly less than 1 in., and this difference is maintained throughout the wetting period of the autumn.]

The prediction for 1939 was not very good: a constant of about 1·7 in. would be needed to obtain a correct prediction. The midsummer running of 1936 was not predicted: the estimated deficit was small at the time (0·67 in.) but not quite small enough to satisfy the alternative definition of 'success' set out above. The autumn, 1936, running was correctly predicted.

The most interesting curves are those for 1933–4. There was no winter running at all, and a short running in May 1934 was not predicted; there was still an estimated deficit of 0·69 in. at the end of April. By a happy chance, soil samples down to a depth of 60 in. had been taken from the field at intervals during 1933 and 1934. Mr. Nicholson, of the School of Agriculture, Cambridge, has kindly placed the field notebooks at our disposal, and from these Dr. R. K. Schofield has estimated the moisture deficits on 12 June 1933, 11 August 1933, and 16 April 1934, assuming that the soil was at field capacity on 7 May 1933 (when the drains were running). There was a number of holes excavated at each sampling, and there is the usual variation from hole to hole, but the main story is quite clear. On 12 June 1933 the deficit was 2·8 in., confined to the top 20 in.: on 11 August the deficit was 5·0 in., extending down to 45 in., the moisture profile in the top 10 in. being the same as in June. The drying probably went even deeper during August and September, winter rain came and brought the surface layers back to field capacity but failed to re-wet the whole profile. On 16 April 1934 the deficit was 2·7 in., the moisture profile showing a deficit of 1·0 in. down to 15 in., a layer at field capacity between 15 and 25 in., and a further deficit of 1·7 in. between 25 and 55 in. This picture may not be quantitatively

true of the whole field, but qualitatively it *is* representative, and it seems clear that a deep dry layer persisted throughout the winter 1933–4, and that by May 1934 only the upper soil had been brought to field capacity. The mole drains being only 24 in. deep would be in this layer and hence would run. The failure to predict the May running as a result of the transpiration estimations cannot, therefore, be set on the debit side of the account; a successful prediction of the running could have been.

The 1933 sampling estimates of the deficit come close to the seasonal deficit curve (see Fig. 2), and one would need to know the distribution of the April 1934 rainfall before being able to decide whether the April estimates (sampling and transpiration) differ by an important amount.

On the whole, the 7 years' results are very satisfactory, as with only one adjustable parameter—the root constant—the running of the drains has been successfully predicted. The adjustable constant is not absolutely arbitrary. It has here a definite physical meaning, and the kind of adjustment made in (10) has a sound biological reason behind it.

(*b*) *The drain gauges, Craibstone, Aberdeen*

The gauges, three in number (I, II, and III), are 1/1,000 acre in area, and consist of blocks of natural soil 40 in. deep enclosed in watertight containers of Caithness slate [4, 5, 6]: daily measurements of drainage water have been taken since 1920. They form small experimental plots differing in manurial treatment, No. III, the subject of the present survey, receiving fertilizers, dung, and lime at various stages during the rotation of crops to which all are subject. The rotation includes a hay crop followed by one or more years of pasture; the present account is concerned with the pasture years only, when the grass was cut short about once a month and was undisturbed by cultivation operations. Tall crops on small plots cannot be considered because they normally intercept more radiation and are better ventilated than an extended area of the same crop would be, and there is more transpiration from them. At Craibstone, for example, the tall hay crops transpire about 25 per cent. more than short pasture because of this extra exposure to wind and sun.

The annual rainfall of about 35 in. is usually sufficient to prevent the development of any extensive deficits in the soil. On the other hand, the shallowness of the soil layer, the coarse nature of the granitic soil, and the frequent cutting of the grass will all tend to make the root reservoir somewhat small. In view of the high rainfall, a general treatment has been applied to the available data. From the records at the observatory, three miles away on the coast, mean values of E_o and E_T were calculated for each month of the year, using long-term mean values of temperature and sunshine [7], and of vapour-pressure and wind-velocity (information kindly supplied by the Harrow branch of the Meteorological Office). The mean estimated transpiration per day appears as the smooth curve in Fig. 3. From the drain-gauge records at Craibstone (made available by the courtesy of the Director, Macaulay Institute, and Mr. Welsh) the mean observed transpiration per day for natural periods [8] was obtained for the pasture years 1930, 1931, 1932, 1938, 1939, and 1940. These periods varied in length from 4 to 94 days. It will be seen that the

main departures from the theoretical curve occur in early and mid-summer. Although the departures are not very great, the smooth curve having fairly faithfully represented the seasonal change in transpiration in phase and magnitude, it seemed worth while examining the weather records in one or two individual years. These, compared with those at Cambridge, reveal generally lower mean air temperatures and markedly

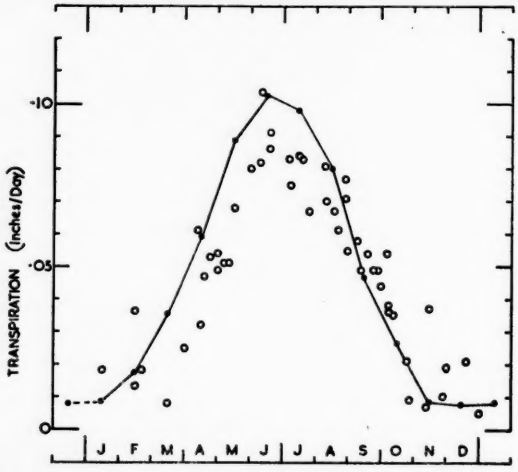

FIG. 3. Estimated and observed transpiration per day at Craibstone, Aberdeen. The full points are estimated from long-term mean weather data: the open circles are observed values for 6 pasture years in the period 1930–40.

lower mean maximum temperatures in spring, suggesting that spring growth, and particularly root growth, might be very much delayed at Aberdeen. There are also, very frequently, months in late spring or early summer with very low rainfall, and these near-drought conditions imposed on turf that has not been able to establish a root system because of low temperatures might lead to partial killing of the grass. Any transpiration estimate, based on weather and the assumption that the grass cover is complete and living, must then be too great. Later in the year, when soil temperatures and rainfall are sufficient to enable complete re-colonization of the plots, the predictions should have the greater accuracy they show in fact.

(*c*) *The drain-gauge, Harrogate*

At one of the reservoirs of the Corporation Waterworks there are maintained, side by side, an open water-tank evaporimeter, 6 ft. square, and a grass-covered drain-gauge, 3 ft. square and 3 ft. deep. The soil of the latter is a filled-in clay, and one would not expect any extensive root development in it. Both gauges are well exposed on a narrow ridge of earth separating two parts of the reservoir. As the annual evaporation from the open water-tank is known to be reasonably close to the estimates based on weather data from Harrogate, the observed values of E_o for the

open water have been used to obtain the values of E_T. As at Aberdeen, summer rainfall is usually sufficiently great to prevent any large deficits from being built up. This, with the filled-in soil, will tend to encourage shallow rooting grasses, and in the rare drought years these may be completely killed, i.e. the transpiration will be stopped and the projecting dead leaves will act as a barrier to evaporation from the soil itself. Thus where a small root constant might be expected on weather and biological grounds, it may have to be given an absurdly low value to account for the death of the grass. A further complication, due to the soil type, is that in dry periods, there may be extensive surface cracking through which rain may pass without first bringing the soil to field capacity. This happens on the bare soil gauges at Rothamsted [8].

With so many qualifications to be made, an extensive application of the treatment of section 2 is not desirable: a table and a diagram will suffice. In Table 1 are given the estimates of the deficit during the drought year of 1921—using two values of the root constant—and the observed monthly drainage.

TABLE 1

Transpiration and Drainage at Harrogate, 1921

Month	Rain (in.)	Deficit at end of month		Observed drainage (in.)
		$C = 3$ in.	$C = 2$ in.	
April . . .	1·26	0·15	0·15	0·23
May . . .	1·85	0·89	0·89	0·01
June . . .	0·17	3·94	3·31	..
July . . .	1·43	4·52	3·59	..
August . . .	3·86	2·62	1·69	0·06
September . .	0·92	3·26	2·33	..
October . . .	1·72	2·38	1·45	..
November . .	2·49	0·12	−0·81	0·84
December . .	3·83	−3·28	−3·40	2·27
January 1922 . .	3·02	..	..	2·71

The smaller constant, $C = 2$ in., correctly estimates the November drainage, and there are reasonable explanations of the earlier runnings which the deficit column does not predict: April drainage was almost certainly due to rainfall at the end of March; May drainage was probably due to a rise in soil temperature, for these small spring dribbles are characteristic of drain-gauges and are caused by a decrease in surface tension of the water in the soil and consequent emptying of some of the full pore-spaces; August drainage was probably due to heavy rain forcing its way through cracks without first bringing all the soil to field capacity. The really serious discrepancy is in December, when the observed drainage was only 2·27 in. for a rainfall of 3·83 in. This was not carried over into January 1922, and, as on no normal basis can one accept a December transpiration of 1·56 in. at Harrogate, one must assume that all the rain that reached the rain-gauge did not reach the soil of the drain-gauge. Normally one has to accept this identity, sometimes with doubts, but here it is apparent that either the rain-gauge collected more rain or

snow than the drain-gauge, or that the drain-gauge was not able to absorb heavy rain rapidly and some was lost by run-off.

Three consecutive normal years are treated in Fig. 4. The deficits were never very large, as rainfall was well distributed throughout the years, and the figure can show little more than the general adequacy of the correction factors used in converting open-water evaporation to

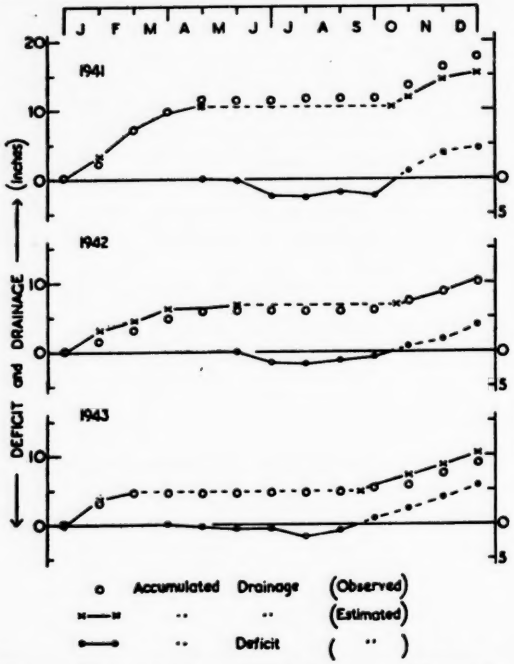

FIG. 4. Observed and estimated drainage at Harrogate.

grass transpiration. The treatment failed to predict running of the gauges in July 1944 (0·38 in.), September 1942 (0·22 in.), and June 1943 (0·20 in.), but the general picture of the seasonal variation in drainage is reasonably good, and predicted annual totals are of the right order.

(*d*) *Drain-gauges in southern England*

At Compton and Farlington, a few miles apart in west Sussex and east Hampshire respectively, there are turfed drain-gauges used by the Borough Engineer to the Portsmouth Waterworks for estimating evaporation losses from the Downs Catchment Area (Compton) and from a typical collection of catchment soils filled into gauges near the settling tanks outside the city (Farlington). The Compton gauge is 3 ft. square and 3 ft. deep, the top 12 in. of soil being loam and the remainder rammed chalk. At Farlington several gauges are in operation: two with which we shall be concerned are 24 and 48 in. deep, the top 12 in. of both being loam soil, and the remainder rammed chalk filled in.

The performance of these gauges would provide excellent material for this survey but for the defect of there being no meteorological observations available in the neighbourhood. The nearest useful stations are at Calshot (16 miles) and Southampton (20 miles) and, in view of Calshot's exposed position on the edge of Southampton Water, the more distant station has been chosen. Use of the Southampton records cannot provide much more than a general indication of evaporation potentials at Compton and Farlington, and discrepancies between observed and predicted performance of the gauges must be expected. As in the case of Cambridge, the most interesting of recent years are 1933 and 1934.

(i) *Compton*, 1933–4. Table 2 shows the observed and predicted behaviour of the gauge, using Southampton weather data and two values of the soil constant.

TABLE 2

Transpiration and Drainage at Compton, 1933–4

Month	*Rain* (*in.*)	*Deficit at end of month*		*Observed drainage* (*in.*)	*Southampton rain* (*in.*)
		C = 3 *in.*	*C* = 4 *in.*		
1933					
May	3·22	0·96	0·96	0·44 (early in month)	1·88
June	2·09	3·08	3·08	..	1·78
July	2·97	4·13	4·26	..	1·72
August	1·17	4·63	5·46	..	0·93
September	2·88	3·61	4·44	..	3·19
October	2·23	2·12	2·95	..	1·87
November	0·90	1·49	2·32	..	0·69
December	0·92	0·62	1·45	..	0·79
1934					
January	2·68	−1·91	−1·08	1·01	2·99
February	..	..	..	..	..
March	..	..	..	..	..
April	2·35	−0·53	−0·53	0·41	2·05
May	0·66	2·66	2·66	0·04	0·83
June	1·92	4·21	4·44	..	1·50
July	1·49	4·61	5·54	..	0·98
August	3·68	3·97	4·90	..	3·54
September	3·07	2·68	3·61	..	2·63
October	2·34	1·10	2·03	..	1·78
November	3·66	−2·33	−1·40	2·63	2·47
December	11·72	−11·65	−11·65	11·19	9·43

Both values of the constant lead to correct predictions of the months of running: values of 4 in. in 1933 and 3 in. in 1934 give good estimates of amounts of drainage, but this change in magnitude is in the opposite sense to that of (10): the season with the wetter spring (1933) requires the larger constant. Speculation about the causes, physical or biological, is profitless in the absence of local contemporary weather data.

(ii) *Farlington, 1933–4.* Table 3 gives corresponding information for two of the Farlington gauges. Whatever theoretical explanation of transpiration is adopted, the performance of these gauges shows a

TABLE 3

Transpiration and Drainage at Farlington, 1933–4

Month	Rain (in.)	Deficit at end of month		Observed drainage (in.)		Southampton rain (in.)
		$C = 2$ in.	$C = 6$ in.	24 in.	48 in.	
1933						
April	1·30	0·73	0·73	0·01	0·04	1·14
May	2·43	1·46	1·46	0·02	0·01	1·88
June	1·65	3·26	4·02	..	0·01	1·78
July	1·67	3·64	6·50	..	..	1·72
August	0·80	3·92	7·50	..	..	0·93
September	3·52	2·26	5·84	..	..	3·19
October	1·80	1·20	4·78	0·18	..	1·87
November	0·56	0·91	4·49	0·11	..	0·69
December	0·80	0·16	3·74	0·29	..	0·79
1934						
January	2·04	−1·73	1·85	1·78	..	2·99
February	0·02	0·38	2·23	0·01	..	0·11
March	2·87	−1·38	0·40	1·40	..	3·20
April	1·99	−0·17	0·23	0·04	..	2·05
May	1·15	2·17	2·40	0·06	..	0·83
June	1·24	3·42	4·86	..	..	1·50
July	0·97	3·45	7·26	0·01	..	0·98
August	2·78	3·47	7·28	0·03	..	3·54
September	2·13	3·12	6·93	..	..	2·63
October	1·84	2·04	5·85	..	..	1·78
November	3·37	−1·10	2·71	1·82	..	2·47
December	8·45	−8·38	−5·67	7·69	5·69	9·43

very marked dependence on depth. Perhaps due to some peculiarity in construction of the gauges, it is apparent that a difference in root constant of 4 in. is needed to account for the difference in drainage. The difference persists throughout the available records (up to 1944), for once winter running has started the behaviour is much the same for both. To a first approximation the difference in the root constants is equal to the difference in winter drainage when both gauges are running freely: for instance, the difference at the end of 1934 is 3·8 in. Values for other years range from 2·3 to 4·6 in., with a mean of 3·3 in.

Once again the absence of local weather data restricts the number of drainage records that it is worth while treating, but it seems reasonable to deduce that at both Compton and Farlington, as at Cambridge, the seasonal variation in transpiration from turf with limited supplies of moisture can be successfully estimated from a meteorological and physical standpoint with the introduction of one arbitary constant. The meaning of the constant is not revealed here as clearly as at Cambridge.

(*e*) *The Harpenden Water Company catchment*

The development of the concepts set out in the introductory section was, as far as possible, made free from local characteristics, but as there are some empirical aspects of the formulae that may be local in their significance, the main purpose of the present survey has been to apply

the concepts away from the Rothamsted locality. A brief return to Harpenden, however, will show another type of application.

The water-supply for the district is pumped up from the underlying chalk formation. Through the courtesy of the Water Company's Engineer, Mr. A. H. Gates, the variations in well-level during 1944–5 have been made available. Taking advantage of Rothamsted measurements of wind speed and short-wave radiation for use in (1) and (3),

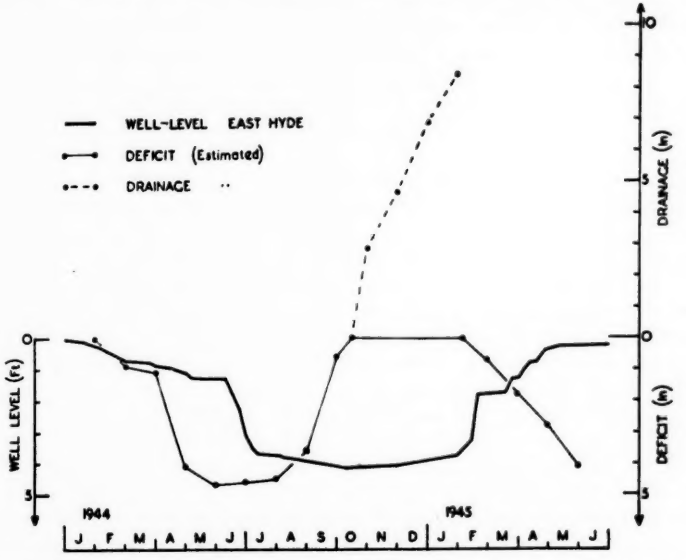

FIG. 5. Fluctuations in well-level at East Hyde. The winter rise begins as the estimated deficit is reduced to zero.

values of E_o and E_T were calculated as for other stations in previous sections. Taking the root constant as 3·5 in. (based on (10)), the seasonal change in deficit was calculated. The plots of well-level and deficit appear in Fig. 5. The relevant point of the figure is that the beginning of the rise in water-table occurred at the middle of October when the estimated deficit was reduced to zero. At this time the first rain would reach the water-table, and presumably the first slight rise in well-level was due to the making up of the deficit in the immediate neighbourhood of the well; it apparently took some months for the effect of rising water-table at the more distant parts of the catchment area to appear at the observation well.

An irrelevant point of the figure, which might give rise to misconceptions if passed over without comment, is the apparent similarity in shape of the two curves. It is exceedingly unlikely that any of the observed fall in well-level was due to transpiration, and the shape of the well-level curve is probably a reflection of the variable value of the specific yield of the chalk. The water-bearing properties of chalk, or rather, its

water-yielding properties, are largely dependent on the nature of the fissures and the interconnexions of fissures, and may change rapidly in short distances both horizontally and vertically.

4. *Discussion*

Assessment of the value of the proposed treatment of evaporation must go back to the basic equations. There are empirical aspects of both (1) and (3), more obvious still in the forms used for practical computation. In the diffusion equation (1), the evaporation-rate depends upon a vapour-pressure difference that becomes very small in winter, and, as errors tend to be absolute, the winter estimates of E_a are less certain than those of summer. In the energy balance, the second term expressing back radiation from the earth is subject to uncertainties because of the difficulty of precise specification of cloud control of the process. This term varies little during the year, and in winter it may be of the same order as the first term; the maximum uncertainty in (4) therefore occurs in winter. In the combination, the estimates of E_o are, therefore, relatively most uncertain in winter, but as the magnitudes are not very great the absolute error may not be serious. Summer estimates of E_a and H are relatively more certain, but as absolute magnitudes are greater, the absolute uncertainty may be of the same order as in winter. The uncertainty over the whole year may be about 10 per cent., that is, estimated annual evaporation from open water may be uncertain to within 2 or 2½ in., and this can probably be shared equally among all months.

The uncertainty is carried over into the estimates of potential transpiration. The ratio of E_T/E_o and its seasonal variation are based on only 2 years' data and may be peculiar to the site and epoch of the experiments. The Aberdeen and Harrogate data, however, suggest that the ratios used are of the correct order of magnitude.

The shape of the drying curve (Fig. 1) and the value of the root constant cannot be completely separated in discussion. For a mixed herbage of deep- and shallow-rooted vegetation it may be difficult to define either of them, but for some time to come it may be desirable to fix the first—as has been done above—on the basis of the known behaviour of bare soil under drying conditions and to assume that the variations in behaviour of plant transpiration from soil to soil and from year to year are due to variations in root development. Not much has been done in the study of root development, and there are obvious inherent difficulties in making observations, but a wider study of the subject, to include the effects of composition, cutting, fertilizer treatment, nature of soil and subsoil, depth of soil and subsoil, irrigation, and drought, would be of great importance and utility outside the transpiration and hydrologic problems considered above.

Whenever transpiration or drainage observations are made it would be highly desirable to have contemporary local meteorological data. This is, of course, not always possible and one is grateful for the enterprise that has provided drain-gauge installations in various parts of the country.

The results of future work may involve a drastic revision of the

treatment of sections 1 and 2, but the present position is not too unsatisfactory: it is encouraging to be able to predict the times and intensities of drain or drain-gauge runnings using only one arbitrary constant. Although in the present account the precise significance of the arbitrary constant has not been clearly established, it has at least a recognizable quality, and future work may show how it can be predicted from soil and/or plant and/or weather characteristics.

5. *Summary*

The evaporation from an open-water surface can be estimated from weather data; the ratio of the transpiration from plentifully watered turf to the evaporation from similarly exposed open water is known as a function of time of year. These results of earlier work are restated and used as a basis for estimating transpiration-rates when optimum water-supply is not maintained. It is assumed that the roots occupy a depth of soil which will yield a definite amount of water at maximum rate. After this amount is transpired the rate is limited by the ability of the lower soil to transmit water, and on the basis of earlier experimental work a composite drying curve is drawn up. With this curve and the relevant weather data it is possible to estimate the seasonal changes in the moisture content of soil under turf. It is shown that the times of the running of the field drains at Cambridge University Farm can be predicted using only one arbitrary constant—the available water in the root zone—which varies from year to year with the spring rainfall. No other collection of records is as satisfactory for testing purposes, but applications to drain-gauge records from Craibstone (Aberdeen), Harrogate, Compton, and Farlington have given generally satisfactory results. The survey shows the great desirability of wider studies of root development as affected by soil type and depth, fertilizer treatment, and weather conditions.

Acknowledgements

Much of the information used in this survey has been obtained from outside sources, and I am greatly indebted to the following: Mr. H. H. Nicholson of the School of Agriculture, Cambridge, Mr. H. Welsh of the Macaulay Institute, Aberdeen, Mr. C. West of Harrogate, Mr. Halton Thompson of Portsmouth, Mr. A. H. Gates of Harpenden, and the Climatology Branch of the Meteorological Office. To Dr. R. K. Schofield I owe thanks for the calculations used in section 3(*a*), and for many helpful discussions.

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SOME NOTES ON THE RECORDING AND INTERPRETATION OF X-RAY DIAGRAMS OF SOIL CLAYS

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WITH A PLATE

Introduction

THESE notes are based on experience gained in the study by X-ray diffraction of soil clays, both at the Macaulay Institute for Soil Research and at Rothamsted Experimental Station. They have reference to certain special points of technique that have proved to be valuable, and to certain features of the X-ray diagrams which do not appear to have received adequate attention. They are presented in the hope that they may be of value to other workers in the same field. Not all the suggestions are original, but it is hoped that adequate acknowledgements have been made where necessary.

Recording Apparatus

First of all, something may be said about the type of apparatus that is necessary. The importance of recording the 'basal' spacings of clay minerals need not be emphasized. Since these are very close to the primary beam it is essential that this region should be clearly visible on the film. The minimum requirement is that the first-order reflection of glycerol-saturated montmorillonite at 17·7 Å. should be easily seen. With a 90-mm. powder camera, using copper radiation, this will be at 3·9 mm. from the primary beam; with a 57·4-mm. camera at 2·5 mm. If the montmorillonite reflection is to be seen easily the photograph ought to be clear to within half this distance of the centre, which means that the 'blind spot' at the centre of the film due to the primary beam must be no more than 3·9 mm. or 2·5 mm. wide respectively. In fact (as will appear later), if useful information is not to be missed, it is desirable to be able to go even closer to the primary beam than this, and on our cameras we aim at making the 'blind spot' only 2·5 mm. wide with a 90-mm. camera. This gives a theoretical value of 55 Å. for the maximum spacing which can be recorded with copper radiation. A 'blank' photograph, given the same exposure as an ordinary photograph, but with no specimen in the camera, should show no appreciable blackening, in this or any other region of the film.

The ordinary commercial powder cameras that are known to us are incapable of meeting those requirements without modification, and it is necessary to use a specially designed camera, or to modify a commercially available one. One of the best-known cameras in this country conforms to the Institute of Physics specification [1], and though this is in many respects admirable, it provides for a large beam-catcher (for suppressing the primary beam) which obliterates the important area near the centre of the photograph. Special cameras are available for

measuring 'low-angle scattering', but these are normally unsuitable for simultaneously recording the ordinary, high-angle lines.

The solution we have adopted is not to use a beam-catcher of the ordinary type (in front of the film), but to allow the primary beam to pass through a narrow slit cut in the film. If the camera is evacuated during exposure (to cut out scattering from the air, which is quite important close to the primary beam, even with copper radiation) and the film is properly centred, perfectly clear photographs can be obtained in this way.

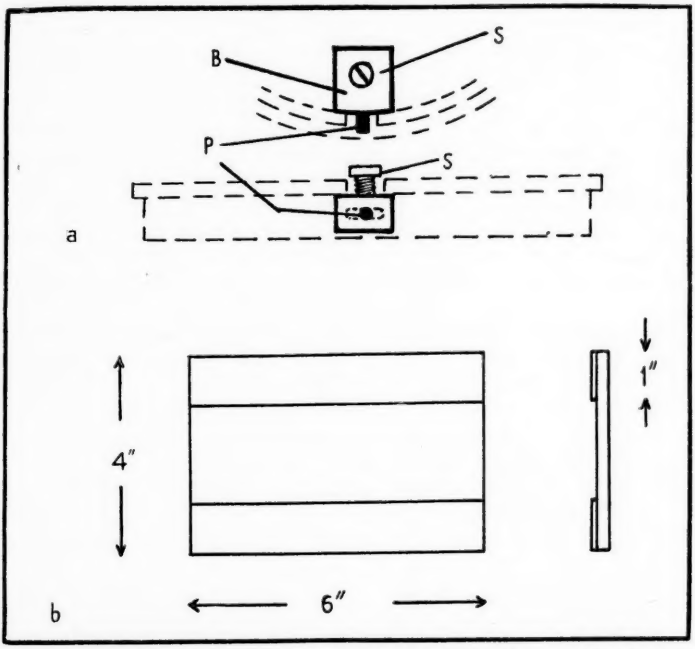


FIG. 1 *a*. Adjustable peg for powder camera. The upper film-carrying flange of the camera is shown in broken line. To make an adjustment the screw *S* is released, the block *B* carrying the peg *P* is moved until the peg is at the required position, and the screw *S* is tightened up again.

b. Specimen rolling device.

The centring of the film is a rather troublesome adjustment, and it is probably because of its difficulty that the solution of using a beam-catcher is so generally adopted. A special punch is made which punches a rectangular slot, together with a circular hole, in the centre of the film (see Fig. 4). The circular hole fits on to a peg which is attached to the camera, so as to locate the slot correctly when the film is fitted into the camera. If the peg is made a permanent fixture there is difficulty in locating it accurately when assembling the camera: it is more satisfactory to make the position of the peg slightly adjustable. This is done by

attaching it to a small block, which is held to the camera by a screw passing through a slot in the top plate of the film carrier (Fig. 1). The peg itself passes through a slot in the circular rim which carries the film. The correct position for the peg is found by fitting a film (with hole, but without slot) on to it, and making a brief exposure. The developed film will show the position of the primary beam with respect to the peg, which can then be moved to the correct position by loosening the screw and sliding the block to which it is attached. It would be easy to think out a more elaborate screw-controlled adjustment of this type, though the simple device described is quite adequate. The adjustment, once made, is permanent.

The primary beam must, of course, be stopped somewhere, and a proportion of it will always be scattered back and could fog the central region of the film. To prevent this a piece of lead, the same width as the film and about 4 cm. long, is glued down to a rigid support, and a hole and slot are made in the centre of it, exactly corresponding to those in the film (or, preferably, the slot should be slightly narrower). This device is fitted behind the film at the time when it is put into the camera. As originally made, and described earlier [2], the lead shield was fixed to the camera cover, but the type of shield described here, which was suggested to me by G. F. Walker, is easier to keep in exact register with the film.

If any fogging of the central part of the film remains after these precautions have been taken, it is probably due to an inadequate collimating system. The slit should be narrow (about 0·3 mm.), and the axis of the camera should be turned so as to make the narrowest possible angle with the target surface, without unduly weakening the beam. A second auxiliary slit placed near to the X-ray set may be necessary to cut out parasitic radiation from other sources than the focus itself. It must be remembered that the collimator slit will act like the pin-hole of a pin-hole camera, and give an image on the film of any extraneous sources of X-rays.

Specimen preparation. Ideally, a true 'powder photograph' of a crystalline substance should show no preferred orientation, i.e. the lines should all have their true relative intensities. With soil clays, which are mostly of predominantly flaky habit, this condition is almost impossible to obtain, and is not really desirable. If the well-known oriented-aggregate technique [3] is used, the basal reflections will be enhanced, sometimes almost to the exclusion of the general reflections. The aggregate may be mounted as suggested in a previous publication [2] to which reference should be made, and moistened with glycerol so that montmorillonite, if present, may be readily identified. If a rather narrow specimen of this type is used, it may be rotated for part of the time of the exposure (after a period of exposure with the specimen stationary, and parallel to the X-ray beam), thus getting both the general lines and enhanced basal reflections on the same film. By this means, which was suggested to me by Dr. Nagelschmidt, the maximum amount of information may be obtained from a single photograph, though the general lines may sometimes interfere with the interpretation of the basal reflections.

Another method which has been used [2] and which gives a similar result, is to mix the clay with a binder, and roll a small portion of the mixture to form a rod about 0·3—0·5 mm. in thickness. This method gives enhanced basal reflections due to orientation of the flakes which occurs during rolling, but it also gives the general reflections (with or without rotation of the specimen).

With the device shown in Fig. 1*b* it is easy to produce specimens of

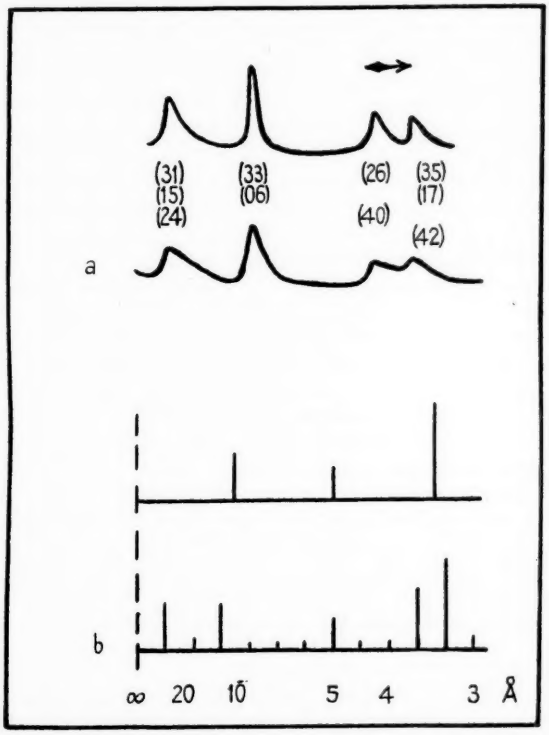


FIG. 2 *a*. Parts of microphotometer records of samples of montmorillonite (above) and halloysite (below). The arrow indicates the direction of increasing θ. The lines are all general (*hk*) lines and have the indices indicated. The sharpness of the (06) montmorillonite line is such that its asymmetrical shape is scarcely noticeable to the eye.

b. A (purely schematic) indication of the sequence of basal reflections from dioctahedral mica (above), and from a hypothetical hydrated mica of period 35·4 Å. The reflection at 8·85 Å. is 'killed' by the rapid fall in the scattering from the mica layers, which occurs in this region.

uniform diameter, and as narrow as may be desired. A sheet of glass is cut 15 cm. × 10 cm., and along the two long edges are cemented strips of thin glass, each 15 cm. × 2·5 cm., of thickness equal to the diameter wanted for the specimen. The thin glass may be of the type used for microscopic cover-glasses, which can be bought in graded sizes, so that

a set of these devices may be made and kept in stock to produce specimens of any diameter required.

In use, a small portion is taken of the clay-binder mixture in a pasty condition, and this is rolled down to about 1 mm. diameter on the palm of one's hand. It is then placed on a plain sheet of glass and is rolled down to the correct final diameter, using the device described above. The specimen is kept in the gap between the spacers while rolling, and gentle pressure applied until it has reached the correct size. If the specimen tends to break up while rolling it means either (*a*) the binder has gone dry, or (*b*) large aggregates are present in the specimen material, which must therefore be further powdered in a mortar.

The question of a suitable binder to use for preparing specimens in this way is rather a difficult one. For many types of powder specimens a mixture of 'Durofix' 10 parts (by volume), glycerol 1 part may be used. The mixture is thoroughly agitated before use to give an emulsion of creamy consistency. The purpose of the glycerol is to ensure that the specimen does not curl on drying and remains pliable. Our experience with this binder suggests, however, that the 17·7 Å. reflection given by glycerol-montmorillonite is liable to be spoilt when it is used, probably because of the organic solvents contained in the 'Durofix' (a photograph of a montmorillonite sample prepared with this binder is shown in Fig. 4*c* of an earlier paper [2]). Indeed since montmorillonite will react with most organic liquids except saturated hydrocarbons, it is obviously difficult to find a binding medium that will be completely inert. A solution of 'Alkathene' in a short-chain paraffin suggests itself, but I have not found it to make a suitable binder.

The best solution seems to be to use a binder which contains only glycerol and water as solvents. This may be made by taking a mixture of about 2 vols. glycerol and 1 vol. water, heating it to the boiling-point, and dissolving ammonium alginate in it until a thick pasty mass is formed. After forming the specimens with this mixture they may be put in a vacuum desiccator to dry out. The specimen thus formed is pliable, but relatively easy to handle when dry, and does not curl during drying. The binder alone does not give any lines.

Interpretation of Photographs

The general technique of measuring and interpreting the X-ray photographs is, of course, well known. But I would like to point out certain features of clay mineral photographs which we have found it advisable to concentrate on initially, when trying to unravel what may be a complicated diagram.

First of all, there are, of course, the basal reflections, full lists of which have been given in several publications, by Sedletskij [4], by Nagelschmidt [5], and in a previous paper of my own [2]. In this connexion it might merely be of value to draw attention to the possibility of making a rather sharp distinction between the Group I and Group II micas (Nagelschmidt [6]), on the basis of the intensity of the second-order reflection at 5·0 Å. (very weak or zero for the latter, medium for the former). The relative strengths of the first three orders of the mica

reflection should enable one to make a reasonable guess at the proportions of the two types.

For soil clays it is probably correct in general to identify the Group I with the 'dioctahedral' [7] (Winchell's [8] 'heptaphyllite'), and the Group II with the 'trioctahedral' (octaphyllite) micas, and these terms will be used in the following portions of this paper.

A feature of clay mineral photographs which has not received as much attention as the basal series of reflections, but which may be a source of very useful evidence, is the (060) and (06) group of lines. Since all the usual clay minerals are based on a similar structural framework, there is a considerable similarity in the diagrams they give. In particular, a strong line with the indices (060) or (06) always stands out in the neighbourhood of 1·5 Å. The position of this line varies according to the composition of the sheets of which the mineral is built up (not according to the spacing *between* the sheets), and the following table indicates its position for the different types of mineral:

1·485	kaolinite.
1·49–1·52	dioctahedral micas and montmorillonites.
1·525–1·535	trioctahedral micas and montmorillonites.
1·53–1·56	chlorites [9].
1·533	chrysotile and antigorite [10].

Often, on photographs of soil clays, two or even more lines may be seen in this region, and these may provide valuable evidence in conjunction with the basal reflections. If, for instance, two types of mica, dioctahedral and trioctahedral, are present, the relative intensity of the two (060) lines will enable an estimate to be made of the 'diocta : triocta' ratio, and this should agree with that deduced from the basal reflections. Again, a 7 Å. line cannot be due to kaolinite unless there is an (060) line at 1·49 Å., but will have to be ascribed to chlorite or chrysotile. Of course, a *complete* identification of all the lines of a diagram will automatically take account of these special lines, but this is not always practicable or necessary; and it would still be useful to pay special attention to these lines for the sake of the clues they may give.

One must, of course, make sure that no other minerals are present which could give lines in the same region, or else make allowance for them. Quartz, for instance, if much is present, can give a line at 1·537 Å., and this might be confused with a triocta-mica reflection. It is often possible to eliminate the quartz by centrifugal fractionation of the clay, rejecting the coarsest fraction. Kaolinite gives a line at 1·539 Å., but this is not likely to give much trouble, as it is considerably weaker and broader than the true (060) line, and is really out of the range covered by most of the reflections of this group. With the less regular 'fireclay type' kaolinitic minerals described by Brindley and Robinson [11], this line is negligibly weak. Some well-crystallized micas and chlorites have another (generally much weaker) line close to the true (060) line, but such minerals are unusual in soil clays.

The technique of measurement must be good enough to distinguish quite positively between a line at 1·49 (say) and one at 1·53 Å. There should be no difficulty in this, because the separation is quite a large one

(see, for example, Fig. 4*h*), and in fact it should be practicable to distinguish readily between different members of the dioctahedral series of minerals, e.g. nontronite (1·515–1·52 Å.) from montmorillonite (1·49–1·50 Å.) [12]. Allowance should be made for the shrinkage of the film by observing the distance between the shadows of calibrated knife-edges [1].

Line Shape

By shape is meant the detailed distribution of blackening in the line across its breadth. Normal powder lines are symmetrical, i.e. the blackening falls away similarly on either side; but if the packing of the structural sheets composing a clay mineral is irregular, the lines may become unsymmetrical, with a sharp inner edge (nearest the centre of the photograph) and a gradual fall of intensity on the outer edge (Fig. 2 *a*). Actually this is the ideal type of distribution given by a series of regular planar arrays of similar atoms, irregularly mingled. In a clay mineral we do not have an array of single atoms, but of groups of atoms (the 'repeating unit'), and since such a group does not scatter X-rays uniformly at all angles (or even give a uniform fall of intensity with angle, as a single large atom would do), its own pattern is superposed on that of the 'two-dimensional lattice'. Brindley and Robinson [13] have calculated in detail the effects to be expected for the clay mineral halloysite, and they show that one may get a sharper fall than would otherwise be found (e.g. for the (06) line), or a rise in the scattering factor of the structural unit combined with the fall due to the lattice may even give rise to a spurious peak outside the main peak (e.g. for the (13, 20) line).

The main importance of these results for clay mineral identification lies in the possibility of eliminating certain minerals, on the basis merely of the shapes of the lines. Montmorillonite and halloysite being composed of randomly stacked two-dimensional layers [14, 15], all 'general' lines belonging to them must be asymmetrical (i.e. except for the basal reflections, which are affected by the separation between layers rather than by the structure of the individual layers). Asymmetrical reflections are not given by well-crystallized minerals like muscovite and kaolinite, but may be given by partially disordered material, such as illites, and the kaolinitic material from some fireclays [11]. Such reflections are thus not necessarily due to montmorillonite or halloysite, but a strictly symmetrical (general) reflection cannot be due to these minerals.

A line of this unsymmetrical type will tend to be displaced from the normal position, in the sense that the spacing deduced from the position of the peak intensity will be smaller than the true spacing. In fact, for the (06) reflections, the error seems to be generally negligible, though it may become important with very broad lines (very small particle size).

Diffuse Basal Reflections and Central Scattering

Sometimes the nature of the basal reflections is such that a simple cataloguing of lines is inadequate. Fig. 4 *a* and *b* show some of the phenomena that may be observed. In *a*, which represents a purely micaceous clay (not a soil clay, but a particularly good example of a type of diagram which has been obtained from several soil clays), the

10 Å. reflection is sharp on the outer edge, but the blackening falls gradually towards the centre (in fact the reflection is asymmetrical like the 'general' lines of montmorillonite and halloysite, but the 'tail' is the opposite way round). In *b* there is a band of blackening from 10 to 14 Å., rather sharply bounded at each end. In each case there is also a marked increase of blackening towards the centre of the photograph. This is a genuine effect, not due to scattering from the apparatus or the specimen support, as is proved by blank exposures (cf. also Fig. 4*i*).

On heating the specimens to 540° for several hours, the diffuse bands disappear (including the central scattering), leaving a sharp line at 10 Å. We may therefore suppose that the diffuse scattering is in each case due to hydration of micas by the introduction of water molecules between the structural sheets. An immediately obvious explanation of the bands would be that in case *a*, as well as the 10 Å. spacing, there occurs a continuous range of spacings larger than 10 Å.; and in case *b*, a range from 10 to 14 Å. This cannot be exactly correct because the expansion of the basal spacing will occur in definite steps, depending on the diameter of the interpolated molecules. If we provisionally assume that hydration results in the introduction of two layers of water molecules, this will give a spacing between one sheet and a corresponding point on the next sheet of about 15·4 Å. (equal to 9·4 Å., the thickness of one sheet, plus 6 Å., twice the diameter of a water molecule). As regards the arrangement of the water molecules there are three main possibilities:

(1) They are regularly interpolated between the mica sheets.
(2) They are interpolated at random.
(3) They occur grouped in certain parts of the crystallites.

Each arrangement will give rise to a characteristic type of scattering near the centre. To consider case 1 first, if we have a regular interpolation of, say, one water sheet to every three mica sheets, the actual 'identity period' (the distance from one point in the crystallite to the next identically situated one) will be 35·4 Å. ($= 2\times 10+15{\cdot}4$). The effect of this on the diffraction pattern will be that the series of reflections will all be strictly at submultiples of 35·4 Å., but that where a reflection coincides, or nearly coincides, with a reflection of the unaltered mica, it will tend to be strong (see Fig. 2*b*). Apart from these special reflections, one would expect only the first-order reflection at 35·4 Å. to be fairly strong, due to its proximity to the primary beam. With one water sheet to four mica sheets, reflections would be at submultiples of 45·4 and so on.

Fig. 3*a* and *b* illustrate the sort of effect to be expected from case 2. The curves give intensity of reflection as a function of the reciprocal of the 'apparent spacing' (for the region covered this is very nearly proportional to the angle of deviation of the beam, i.e. to the distance as measured on the film), for various values of *f*, the 'degree of hydration' (not the percentage hydration, but the proportion of hydrated sheets to the total number of sheets in the crystal). The curves are calculated from the formula derived by Hendricks and Teller [16] for X-ray scattering due to random mixtures of layers.

It will be seen that these curves, in the case of moderately hydrated material ($f < 0{\cdot}15$), suggest (i) a rather sharp reflection in the neighbour-

hood of 10 Å.; (ii) a general diffuse background *inside* the 10 Å. line (for the case $f = 0{\cdot}2$, this type of diagram passes into one showing almost uniform blackening extending out to 10 Å. with a rather sharp cut-off at this point); and (iii) a rise in scattering near the centre, starting at about 25–30 Å. apparent spacing. On glycerol treatment the 10 Å. reflection is sharpened.

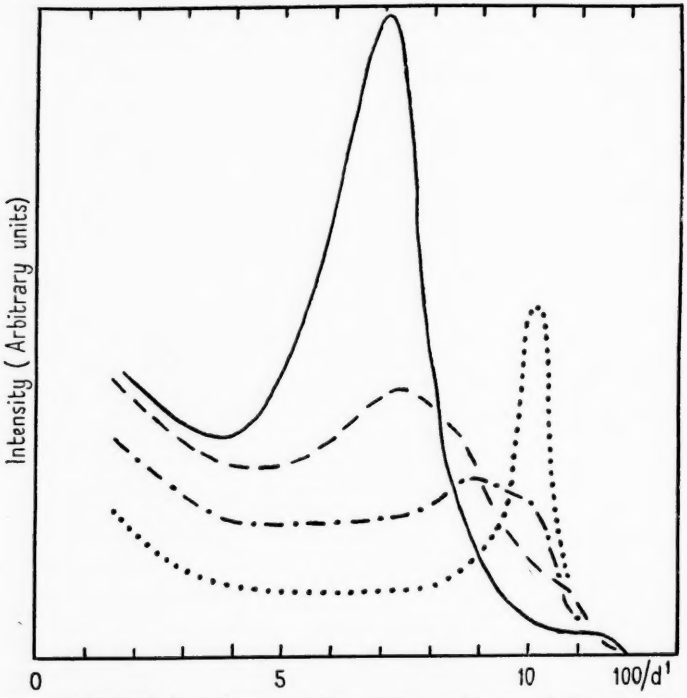


FIG. 3 *a*. Calculated intensity curves for random mixtures of dioctahedral mica layers (period 10 Å.), and the same layers hydrated (period 15·4 Å.).

Case 3 will merge, on the one hand, into case 1 (when definite regions of uniform constitution are present in the crystallites), and, on the other hand, into case 2. As an intermediate case we might have for instance the state of affairs represented in Fig. 3 *d*, where there is a more or less unaltered core, and a gradually increasing hydration towards the outside of the particle. Such a structure would give a sharp 10 Å. reflection due to the core, with a series of overlapping satellite bands of increasing mean spacing due to the hydrated shells. Corresponding to these there would be high-spacing bands near the centre. The bands on the low-spacing side of the 10 Å. line would be extinguished because the scattering factor of the mica sheets drops rapidly to zero in this region. The exact shape of both the satellite band to the 10 Å. line and the band of central scattering would depend on the relative proportions of material

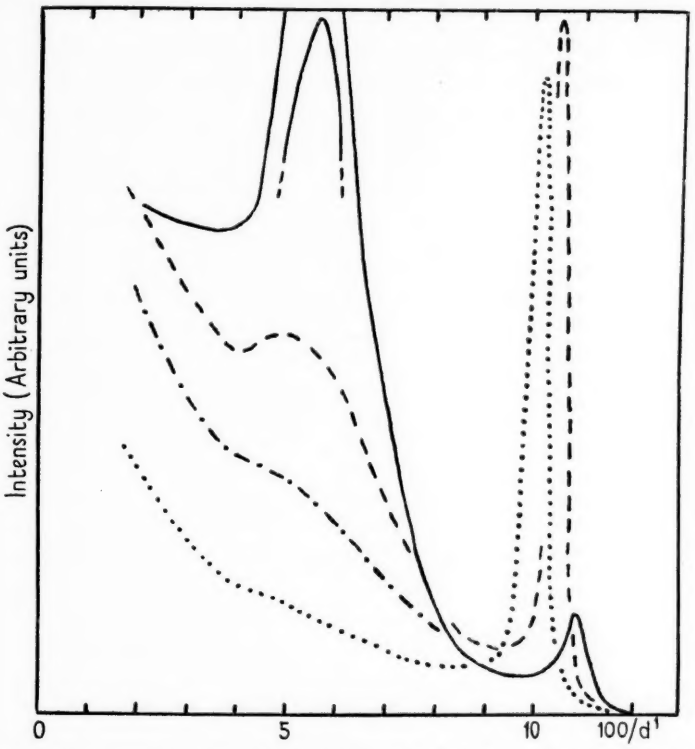


FIG. 3 *b*. Corresponding curves for mixtures of 10 Å. and 17·7 Å. layers (as obtained by glycerol treatment of montmorillonitic material). The right-hand sharp peak of the $f = 0{\cdot}2$ curve is omitted to avoid confusion.

——— $f = 0{\cdot}5$ —·—·—·— $f = 0{\cdot}2$

– – – – $f = 0{\cdot}3$ ····· $f = 0{\cdot}1$

(where f = proportion of hydrated or glycerolated sheets).

The curves have been calculated from the following formula:

$$I = (F_1^2)\left(\frac{2-\sin^2 2\theta}{\sin 2\theta}\right)\left(\frac{2f(1-f)\sin^2\pi\frac{d_2-d_1}{d'}}{1-2f(1-f)\sin^2\pi\frac{d_2-d_1}{d'}-f\cos 2\pi\frac{d_1}{d'}-(1-f)\cos 2\pi\frac{d_2}{d'}}\right)$$

where θ = Bragg angle of reflection, d' = 'apparent spacing' (as measured from photograph), and d_1 and d_2 are the spacings of the two types of sheet.

The first bracketed term is the scattering power of the structural sheets (calculated, neglecting the adsorbed molecules and the K ions). The second represents the ordinary change in intensity of the scattered X-rays with angle due to geometrical factors (the particular formula used is that appropriate to a single crystal, which was thought most suitable for the case of an oriented aggregate). The third term is derived from the formula given by Hendricks and Teller [16] at the end of section 2 of their paper, for the case of only two components (the transformation is due to J. Méring, and was obtained from a communication given by him to the 'Groupe des Argiles').

of different stages of hydration, but we should expect a general similarity in shape between them.

It seems likely that all the types of arrangement exist in soil clays, and can give rise to the central scattering and diffuse bands which are

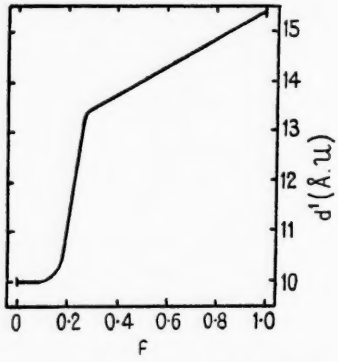


FIG. 3 *c*. Variation in position of the '(001)' peak with *f*, for the hydrated mica. Between $f = 0{\cdot}1$ and $f = 0{\cdot}3$, the peak is diffuse (see Fig. 3 *a*).

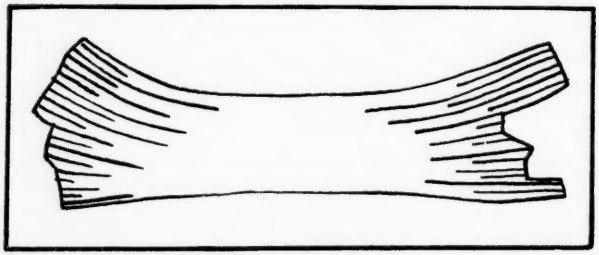


FIG. 3 *d*. A possible way in which regions of varying degrees of hydration could occur in a mica crystal (the lines represent layers of water molecules).

observed. Fig. 4 *a* can be fairly adequately accounted for on the basis of random hydration with $f = 0{\cdot}15$ approximately; but the central scattering is perhaps rather more intense than would be caused by such an arrangement, and the effect of glycerol in sharpening the 10 Å. reflection is not obvious. Probably, therefore, the hydration is not completely random. In Fig. 4 *b* the effects of type 3 hydration probably predominate, with a tendency towards type 1. Here both diffuse bands have a rather sharp limit. The patch of central blackening ends sharply at about 25 Å., the outer band extends from 10 to 14 Å., with a peak at 12 Å. (the 14 Å. peak is partly due to chlorite). It appears that the sample is altering towards a vermiculitic material of spacing 14 Å., and contains rather a large proportion of material in which fully hydrated layers are alternating with normal mica layers. In fact, in this photograph, careful examination shows a definite peak at 24–5 Å. Another photograph of this type (not illustrated) shows clear peaks at 24 and 34 Å. Often, however, such

peaks are absent and both the central scattering and the 10 Å. satellite take the form of diffuse bands, rather sharply bounded (Fig. 4 *c*).

Sample *b* is a trioctahedral mica, sample *a* is dioctahedral, as can be seen both from the sequence of basal reflections and from the (060) lines; in the case of the Scottish soil clays investigated by me these types of diagram seem to be rather characteristic of the two types of mica respectively. The trioctahedral variety may also show a reflection at about 12 Å. with moderate central scattering, as in Fig. 4 *d*. This can probably be accounted for on the basis of a random mixture of 10 and 14 Å. units, since there is no definite peak at 24 Å. In what appear to be the initial stages of alteration of trioctahedral mica it is also possible to get an appearance like that of Fig. 4 *a*, though both the central band and the diffuse tail to the 10 Å. line are less marked. On heating to 540° both disappear. Apparently the trioctahedral mica tends towards a stable form with probably two layers of water molecules between the mica sheets, and a spacing of 14 Å., which is unaffected by glycerol (it should be noted that the samples illustrated here, except 4 *a*, were treated with glycerol as a standard procedure). There is also an intermediate stable form with (approximately) alternate hydrated and non-hydrated mica sheets. The dioctahedral micas have not shown evidence of such clearly defined stages, and they possibly alter to a swelling material resembling montmorillonite rather than to a vermiculitic material. This is suggested by Bradley's [17] description of a hydrated dioctahedral mica ('bravaisite') in which there is a random alternation of montmorillonite-like (i.e. swelling) and mica-like parts. Our material is less hydrated than this (and probably not so uniform), but the hydration process may be rather similar.

Fig. 4 *h* is a photograph of a kaolinitic material which shows an almost uniform region of central scattering, with a rather sharp outer edge at 7 Å. This is a particularly good example of a type of diagram which has also been obtained with micaceous minerals, and corresponds to a random hydration with $f = 0{\cdot}2$ approximately (see Fig. 3 *a*). With the micaceous minerals the cut-off would, of course, be at 10 Å. The sample illustrated also contains some trioctahedral mica, and the two (060) lines can be seen very clearly.

Fig. 4 *e* and *f* are given as a further illustration on the theme of central scattering. They represent a montmorillonitic clay which has been activated by treatment with dilute mineral acid, *e*, in hydrated condition, and *f*, after drying (samples prepared by Dr. B. S. Emödi). The first photograph shows a sharp basal reflection corresponding to about 18 Å., with only a little central scattering, the second a diffuse reflection having its peak at about 11·4 Å., and strong central scattering. The explanation seems to be that the spaces between some of the montmorillonite sheets are partially filled with products of the decomposition of the clay, so that after dehydration an irregular structure is produced like that suggested for the soil clays. On hydration the irregularities disappear by the filling-up of the gaps with water molecules. In the case of the soil clays previously mentioned, dehydration by heating removes the central scattering; in this case it increases it. This reflects the fact that in the one

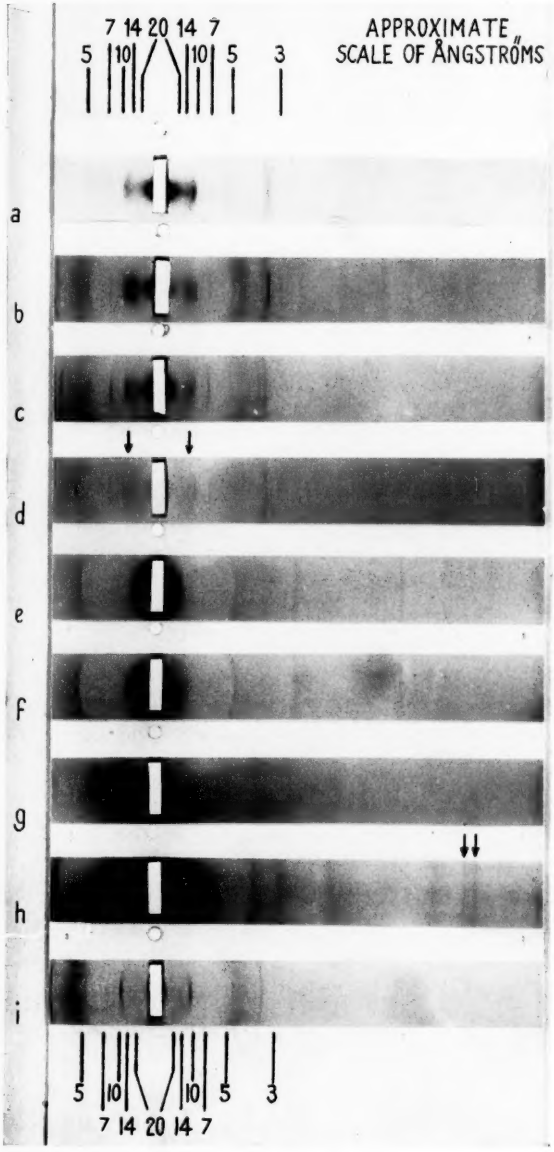
case the irregularity is due to water molecules, in the other case to solid products which are not removed by heating.

Fig. 4*g* shows that this second type of irregularity may also occur in soil clays. It represents the clay from another soil after heating to 540° C. Before heating, this clay gave a rather sharp reflection at 14 Å., with little central scattering. The result of the heating has been to increase both the central scattering and the diffuseness of the basal reflection of the micaceous mineral, as well as moving the latter towards the 10 Å. region. It seems that in this case the 14 Å. reflection originally present does not represent a pure hydrated mica, but that there is some material irregularly distributed between the mica sheets which prevents them from coming completely in contact when the water is expelled. The exact nature of this material remains to be established, but as there is a relatively high amount of free iron and aluminium oxides in this soil, which is derived from a basic rock (norite), it seems probable that the material is of this nature rather than amorphous silica. 'Partial chloritization' might be a suitable name for the phenomenon in this case. In this connexion, it is interesting to note that Caillère, Hénin, and Méring [18] have shown that a partially chloritized material may be formed from montmorillonite by chemical precipitation of magnesium hydroxide between the structural sheets. The central scattering suggests that the chloritization, in our case, is less regular than in their material. The case is similar to that illustrated in Fig. 3, except that initially there is little difference in the spacing of the sheets, but only in the amount of foreign material present between them; and only after heat treatment is this difference reflected in spacing irregularities.

Conclusion

It is hoped that this brief review of a few clay mineral photographs will have served to convince investigators of soil clays using X-rays that there is much information of value to be obtained by examination of the whole diffraction photograph, up to as near the centre as can be attained, and that it is worth while to pay careful attention to technique so that nothing may be passed over. When a large number of clays has to be examined, of course, the chief problem will be to combine good technique with the most expeditious way of working. For this, as much information as possible should be recorded on one photograph. There is no reason why, using the type of apparatus suggested, a good record should not be obtained from 50 Å. to about 0·8 Å., using copper radiation, with an exposure of 1½–3 hours. This range really extends too far at the low spacing end, and chromium radiation, giving a spacing range of 75 Å. to 1·2 Å. is preferable, and also has the advantage of bringing the important (060) lines to a position where the sensitivity of measurement is greater.

The photographs used in illustration of this article were obtained while I was working at the Macaulay Institute for Soil Research, Aberdeen. Clay mineral analyses based on some of them have already been published [19].



a. 'Athi bentonite' from Kenya (a hydrated dioctahedral mica). Oriented aggregate.

b. Clay from A_2–B horizon of Achnashellach podzol A13 [19]. This soil is derived from schist. Glycerol treated oriented aggregate. The photograph is slightly asymmetrical, and the central blackening is most distinct on the left side.

c. Clay from Tiendland soil derived from Old Red Sandstone sandy gravel. Glycerol treated oriented aggregate.

d. Clay from B_2 horizon of Achnashellach soil A11 [19] (derived from schist). Glycerol treated oriented aggregate.

e. Activated montmorillonitic clay, hydrated. Powder photograph (specimen in glass tube).

f. The same, dried.

g. Clay from a soil of podzolic type (Muir), derived from norite, after heating 5½ hours at 540° C. Oriented aggregate.

h. Fine fraction of clay from C horizon of Wester Fingask soil. Powder photograph (specimen rolled with 'Durofix' and glycerol as binder).

i. Clay from Achnashellach soil after heating for 5½ hours at 540° C. For comparison with *b*, *c*, and *d*—note absence of central scattering. Oriented aggregate.

FIG. 4. X-ray photographs of clays. All are taken with copper radiation except *g* and *h* which were taken with iron radiation (to which therefore the Å scale does not apply).

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AN X-RAY DIFFRACTION STUDY OF HUMIFICATION

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HUMIFICATION is the first stage of a slow process whereby vegetable debris is converted into peat, coal, anthracite, and finally into macrocrystalline graphite. The vegetable debris contains initially a diversity of chemical compounds, and as Waksman [1] has pointed out, soil humus, which represents a very early stage of humification, must also consist of a complex mixture of chemical compounds. Since, however, the end-point of humification and coalification is a single chemical entity, viz. macrocrystalline graphite (certain meta-anthracites give X-ray powder photographs which show a well-developed graphite pattern), then it appears reasonable to suppose that during these changes there is a tendency towards the formation of chemical structures which become more and more alike as the slow process progresses: although intermediate stages may show a range of chemical composition, their classification together as *humic acids* and *humins* is justifiable on the grounds of certain specific characteristics and also is not contrary to the ideas of modern crystal chemistry. Waksman has pointed out that most of the investigations into the chemical properties of humus have been carried out on materials obtained from either peat or coals and, therefore, the results obtained should not be applied indiscriminately to the humus obtained from soils. Artificial humic acids can be prepared by a variety of methods, and although the products show a certain similarity to those from natural sources, there is no proof of close physical and chemical similarity. According to their behaviour with aqueous alkali, humic substances are now usually classified as *humic acids* and *humins*; the former are easily soluble in cold aqueous alkali, whilst the latter dissolve only on heating. The different alkali solubility of the humins has been interpreted by Marcusson [2] in the sense that these substances are dehydration products or anhydrides of humic acid. The decrease in the solubility in aqueous ammonia which occurs when the acids are dried at 105° C. has been ascribed to an alteration in the colloidal state, rather than to anhydride formation. The composition of humic acids obtained from peat and brown coal is not as constant as that of a well-defined chemical compound, but in many cases it approximates to the empirical formula $C_5H_4O_2$. In an investigation of Italian brown coals Ubaldini [3] found that carboxyl acidity is a function of their degree of humification: it increases with the extent of the transformation of the original vegetable matter into humic substances and subsequently decreases gradually with the process of coalification. Phenolic groups, on the other hand, are already present in the parent organic matter of the brown coals, and the proportion decreases gradually during the humification process: they are still present in significant amounts in coals of rank intermediate between brown coals and bituminous coals. Ubaldini suggested the following approximate formula for humic acid:

$$C_{78}H_{52}O_5\begin{cases}(COOH)_8\\(OH)_7\\(CO)_2\end{cases}$$

Other equally complex formulae have been suggested, e.g. Fuchs [4] put forward the formula: $C_{59}H_{35}O_{27}N(COOH)_4(OH)_3(CH.CO)$.

The above brief summary gives an idea of the molecular complexity of these substances. Differences in chemical composition are to be expected among complex, colloidal substances of this type, which have a high molecular weight: they would not be expected to conform exactly to the law of constant composition as it is only strictly applicable to compounds which consist of relatively simple, volatile or soluble molecules. Many other examples could be cited of complex substances showing relatively wide variations in chemical composition yet possessing the same general physical and chemical properties. In the case of the humins and the humic acids, it is probable that the exact quantitative aspects of such properties as base-exchange and adsorptive power are of greater significance than variations in chemical composition.

A detailed X-ray diffraction study of carbonization and coalification has shown that the crystallographic changes which occur during these processes are similar, in spite of the great differences in the rate at which they have occurred, and there is evidence also that the early stages of the carbonization of certain organic compounds resemble humification. For example, Hofmann and Sinkel [5] have shown that the products obtained by charring sucrose at temperatures up to 300° C. show definite base-exchange properties; e.g. about 300 milli-equivalents of hydrogen ion per 100 gm. of the char, compared with 250 milli-equivalents for a specimen of humic acid (Merck). With temperatures of charring higher than 300° C. the base-exchange properties of the product decreased rapidly. Hofmann and Sinkel suggested that the acid properties of the char must be due to the presence of carboxyl and phenolic hydroxyl groups. A deep brown colloidal solution was obtained on treating the char with aqueous sodium hydroxide, pyridine, or acetone: hydrocarbons such as benzene or petroleum ether, on the other hand, did not dissolve anything from the sugar char. The soluble and the insoluble fractions had similar compositions (about 60 per cent. carbon and 2·8 per cent. hydrogen) and also gave similar X-ray powder photographs.

The above results suggest that knowledge of the crystallographic structural changes which occur during carbonization might provide some information as to the nature of these highly complex substances, the humic acids and the humins. The various kinds of amorphous carbon, brown coals, bituminous coals, anthracites, peats, pitches, and bitumens all give similar X-ray powder photographs, which are not unlike those given by humic acids and humins. Debye and Scherrer [6] concluded from the position of the diffraction maxima and the breadth of the diffractions, in the X-ray powder photographs of soots, that amorphous carbon is merely graphite in an extremely fine state of subdivision, so fine, in fact, that it could never be reached by the mechanical comminution of macrocrystalline graphite. The structure of graphite is built up from carbon atoms arranged in a honeycomb pattern in flat layer-planes, stacked parallel to each other in an ordered manner. The carbon atoms within the planes are 1·415 A.U. apart and the layer-planes 3·35 A.U. apart. The broadening of the diffractions in the powder

photographs of amorphous carbons is explained by the minute size of the crystallites present and their consequential low resolving power for X-rays. Further work has shown that although this view of Debye and Scherrer may account for most of the properties of soots and carbon blacks, it does not adequately explain the properties of chars and cokes. A single X-ray powder photograph of one of these highly disordered carbonaceous substances gives little information concerning its structure. From it we can make certain tentative conclusions concerning the preponderating lattice spacings and also concerning the average dimensions of the colloidal crystallites which make up the specimen. Systematic study [7] of the variations of the diffraction broadening which occur in related series of cokes, chars, and coals has given a deeper insight into the structural characteristics of these substances. By measuring the progressive changes in the half-peak widths of the diffraction bands (i.e. the width at half the peak intensity of the band on the micro-photometer trace of the powder photograph), it is possible to follow the development of crystallographic order during both carbonization and coalification. The results of such measurements can be expressed in terms of the diameter (*a* dimension) and the height (*c* dimension), of an average, hypothetical, cylindrical crystallite. The inner, more intense halo of the powder photograph gives the average *c* dimension, and the outer, less intense halo gives the average *a* dimension. The corrected half-peak width of the inner diffraction is related to the *c* dimension (L), by the formula [8], $\beta = 1{\cdot}0\lambda/L\cos\theta$, where λ is the X-ray wave-length and θ the Bragg angle of the diffraction maximum: the half-peak width of the outer diffraction, which is a cross-lattice diffraction, is related to the *a* dimension by the Warren [9] formula $\beta = 1{\cdot}84\lambda/L\cos\theta$.

Four different types of crystallite growth curves have been recognized [10]; these are shown in Fig. 1 where the average *a* and *c* dimensions of the hypothetical, average, cylindrical crystallites are plotted against their respective carbonization temperatures. Fig. 1*a* shows the curves obtained when pure cellulose is used as the parent organic material. The initial increase in the *a* dimension (i.e. experimentally the sharpening of the outer diffraction halo) has been interpreted as due to the progressive lamellar growth of the hexagon layer-planes of the minute graphite nuclei, brought about by the process of aromatic condensation. Chemical studies [11] have shown that this aromatic condensation, or aromatization, commences at a temperature as low as 200° C. The products obtained by charring cellulose in nitrogen, the temperature being raised at 5° per minute, have to be heated to about 400° C. before the diffraction photograph shows clearly the pattern typical of amorphous carbon. In contrast to this progressive growth of the *a* dimension, the constancy of the *c* dimension is surprising and suggests that the layer-planes of the individual crystallites are, in some way or other, rigidly cross-linked. It should be remembered that these chars do not consist of pure carbon, but also contain appreciable proportions of oxygen and hydrogen and that it is only when the carbonization temperature has been well over 1,000° C. that the product approximates to pure carbon. There is evidence that it is this foreign oxygen (and possibly also in some cases,

nitrogen and sulphur) which plays an important role in the formation of these apparently rigid, minute crystallites. The carbohydrates, cellulose, starch, sucrose and glucose (and probably others), lignin, wood, natural and artificial humic acids, certain proteins, and many other

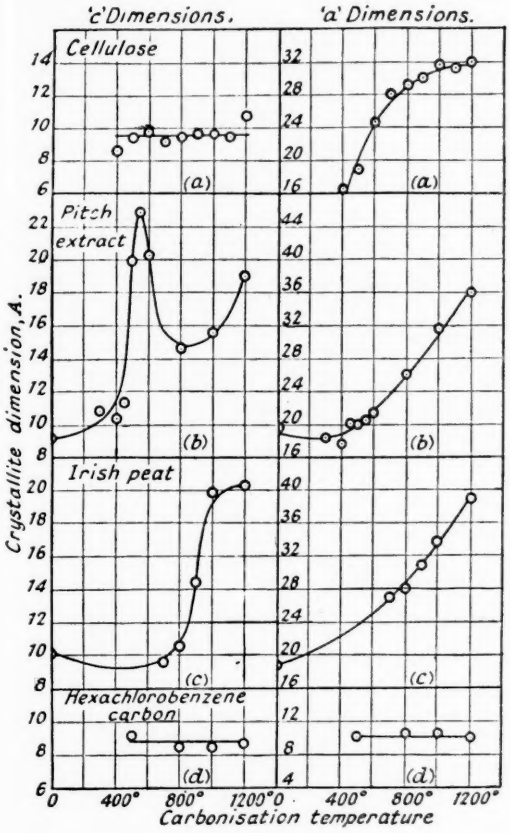

FIG. 1

organic compounds, all containing a relatively high proportion of oxygen, all give chars on carbonization which contain crystallites with average *c* dimensions between 9 and 10 A.U. The carbonization conditions can be varied between wide limits, with respect to both temperature (up to at least 1,200° C.) and speed, without any consequential change in the half-peak width of the inner, more intense diffraction of the powder photograph of the resulting char.

Perhaps the most convincing evidence in support of this hypothesis of the importance of the proportion of oxygen in the parent organic material is that certain aromatic compounds which contain a much

smaller proportion of oxygen give an entirely different type of *c* dimension curve. Fig. 1*b* shows the *c*-dimension curve obtained by carbonizing that part of a bituminous coal pitch which is soluble in carbon tetrachloride. This type of curve is characteristic of systems which contain initially, large, stable, lamellar, aromatic molecules in which there is a small proportion of oxygen: it has been interpreted as follows: The ascending part of the curve, between room temperature and about 550° C., suggests the occurrence of a unidimensional crystallization, brought about by the progressive stacking together of thermally stable, lamellar molecules. The maximum at about 550° C. reflects the completion of the conversion of a system which initially consisted of independent, stable organic lamellar molecules, held together by weak dispersion forces (molecular lattice), into one which consists of rigid (cross-linked) 'carbon' crystallites. Other systems which contain polynuclear, thermally stable, lamellar aromatic molecules which contain some oxygen, e.g. coking coals, bitumens, pure compounds like dibenzanthrone, all give *c*-dimension curves of this type. The interpretation of the subsequent course of this type of *c*-dimension curve is still somewhat obscure and will not be discussed here.

A still further type of *c*-dimension curve is shown in Fig. 1*c*; it is characterized by an abrupt increase in the average *c* dimension in the temperature range, 800–1,000° C. Peats, and to a less pronounced degree, brown coals and lignites give this type of curve; so far, among laboratory-prepared substances, the only ones which have been found to behave similarly are bituminized cellulose and lignin, i.e. cellulose or lignin which has been heated in an autoclave to about 300° C. in the presence of an excess of aqueous sodium hydroxide. If peat (but not bituminized cellulose) is boiled with 2 per cent. aqueous hydrochloric acid and then carbonized, the chars do not show the pronounced increase in the *c* dimension, but like cellulose chars give constant *c* dimensions up to at least 1,200° C. An asymmetry of the photometer trace of the inner diffraction halo of peat chars prepared at temperatures above 800° C. suggests that two types of crystallite are present, the one similar to those in cellulose chars, and the other having a *c* dimension about twice as great. The crystallite growth between 800° and 1,000° C. is so pronounced as to suggest the occurrence of some profound atomic rearrangement in this temperature range, perhaps even a kind of polymorphic transformation. Neglecting the finer points in the lattice structure of microcrystalline carbon, such as the variation in the *c* spacing and the turbostratic stacking of the layer-planes, only two lattice structures of carbon atoms are known, viz. the three-dimensional, covalent diamond lattice, and the aromatic, semi-metallic, layer-lattice of graphite: nevertheless, there is a third possible arrangement of carbon atoms which is shown in Fig. 2. The disappearance, in this structure, of the flat layer-planes suggests that its resonance energy will be less than that of the corresponding graphite lattice, and its existence, therefore, less probable. The lattice contains, however, an orderly network of conjugated double linkages running throughout the whole structure, and its resonance energy would therefore be of an appreciable magnitude.

The existence of such an arrangement of carbon atoms is suggested by the results obtained by Karle and Brockway [12] in an electron-diffraction study of the structure of *o*-tetraphenylene: the non-coplanarity of this compound was established, and the structure suggested, if repeated in three dimensions, would build up the lattice illustrated in Fig. 2. Further experimental evidence of the existence of this type of carbon

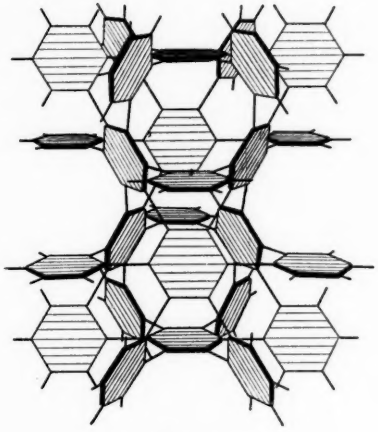

FIG. 2

structure has been obtained from the X-ray study of carbons prepared by treating hexachlorobenzene with sodium amalgam at about 300° C. The X-ray powder photographs, although similar to those given by chars, in that the diffractions are highly diffuse, nevertheless differ in several important respects. On further heating these carbons up to 1,200° C. no change in either the *a* or *c* dimensions was observed (see Fig. 1*d*). Carbons having similar crystallographic properties can be prepared by other methods; e.g. by carbonizing barium mellitate and extracting the barium carbonate formed from the residual carbon, by means of hydrochloric acid. Such carbons are highly adsorptive and possess extremely great accessible surfaces, greater, in fact, than any yet reported. They are, however, only colloidally crystalline, and it is possible that the impurities present, viz. oxygen and hydrogen, play some part in stabilizing this type of aromatic, three dimensionally cross-linked structure. The high adsorptive power and the open lattice structure of these carbons is reminiscent of the skeleton lattice structure of certain zeolites.

Such, then, are the four different types of crystallite growth curves which these carbonization studies have revealed. The results indicate that low-temperature chars and cokes, residual coal (i.e. the residue which remains when the bitumens are extracted from coal by means of organic solvents: mild oxidation converts it into humic acids), humins, and humic acids are structurally closely related. They differ essentially from the bitumens which organic solvents extract from coal: these may

be either paraffinic or aromatic, but are essentially much simpler structures. It is not possible at present to state precisely the structural character of humic acids and humins; probably a large number of related structures are involved, as the above considerations appear to indicate a certain amount of latitude in the molecular architecture of these complex bodies. Nevertheless, the following tentative conclusions are, perhaps, permissible:

1. The average size of the diffracting unit in humic substances is probably of the order of 10×20 A.U., i.e. well within the range of colloidal dimensions. These dimensions should not be regarded as those of a discrete crystallite but rather as representing the statistical extent of a domain of crystallographic order.
2. The degree of aromatization (including perhaps heterocyclic ring systems) increases with the rank (proportion of carbon) of the particular sample.
3. The acidic or base-exchange properties are probably determined by the number of accessible carboxyl and phenolic groups present.
4. The structure is probably either actually or potentially cross-linked. It is not yet possible to be precise about the character of the cross-linking: it almost certainly involves oxygen atoms and possibly also, in certain cases, the tilted benzene rings, as shown in Fig. 2.
5. The structures probably contain both lamellar and cross-linked domains, varying in extent according to the nature of the parent organic material.
6. Little experimental work has been done on the adsorptive properties of humins and humic acids: the very high adsorptive power of the carbons made from hexachlorobenzene, probably brought about by the open structure shown in Fig. 2, suggests that this type of structure may be of importance in determining the adsorptive properties of humins and humic acids.
7. The extent of aromatization and oxidation which the parent organic material has undergone will probably have an important influence in determining the magnitude of both the base-exchange properties and the adsorptivity of the humic acids and humins.

In conclusion it is suggested that perhaps one of the simplest methods of determining the part played by these structurally very complex humins and humic acids would be to employ synthetic materials, characterized not only by chemical composition, which may not be very important, but also by base-exchange capacity and adsorptivity. Just as the nature of amorphous carbon is influenced by the parent organic material from which it is formed, so it is reasonable to suppose that the character of humins and humic acids will be similarly affected.

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THE MOVEMENT AND PRECIPITATION OF IRON OXIDES IN PODZOL SOILS

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THE movement of iron from the A horizon and its precipitation in the B horizon of a podzol profile still leave many unsolved problems in spite of the voluminous literature on the subject.

Iron may move as

(i) a trivalent inorganic cation,
(ii) a divalent inorganic cation,
(iii) a positively charged iron-oxide sol,
(iv) a negatively charged silica-protected iron-oxide sol,
(v) a negatively charged humus-protected iron-oxide sol,
(vi) a complex organic ion.

The movement of iron in the ionic state as a trivalent cation will be limited to very low pH values, the solubility of ferric ion above 3·5 being very small.

In absence of air the solubility of ferrous ion is appreciable over the pH range of soils, but under normal conditions in the absence of waterlogging the ferrous ion in soil is quickly oxidized to the ferric condition and is therefore precipitated. Recently Winters [1], from the results of his experiments with bentonite, gelatin, and other gels, has suggested that iron may move in soils by surface diffusion of ferrous ion within the gel and an exchange reaction with the gel particles. To interpret the movement of iron in podzol soils on this view it is necessary to assume that the gels are continuous throughout the profile and also that the movement only takes place under reducing conditions when the soil is saturated with water. Iron may also move in the ferrous state by percolation in soil solution, provided the soil is saturated with water and anaerobic. The formation of laterite soils and of gley horizons in podzolic soils may depend on such movement, but in normal podzol soils the conditions are generally aerobic.

The movement of iron as a positive iron-oxide sol in association with alumina and humus has been suggested by Mattson and Koutler-Andersson [2]. This cannot be established unless it is shown that the A horizons of podzol soils are positively charged. The authors gave no data on this point, and no one else seems to have found a podzol soil having a positive charge.

The movement of iron as silica-protected iron-oxide sol has been suggested by Reifenberg [3]. The peptizing action of silica is effective in alkaline solution and also at a slightly acid reaction, but at pH 4·0 there is little peptization by silica. Barbier [4] found that about thirteen parts of silica are needed to peptize one part of ferric-oxide sol, though he did not discuss the effect of changing concentration and reaction. In the podzolization process it is most unlikely that there could be such a high ratio of silica to iron oxide in the peptized sols because silica would then

be removed from the A horizon more rapidly than iron, which would thus tend to accumulate in the A horizon. Peptization of iron-oxide sol by silica is a possible mechanism for the formation of 'terra rossa' over limestone in the Mediterranean climates, but it cannot explain the movement of iron in podzols.

The view that the movement of iron takes place as negative iron-oxide sols protected by humus still finds many supporters. Aarnio [5, 6] did pioneer work on the mutual reactions of iron-oxide sol and humus sol, and his work has generally been quoted in subsequent discussions of this subject. However, the effects of the concentration and reaction of the sols on their mutual coagulation were not studied either by Aarnio or by later workers, such as Udulft [7], Simakov [8], and Winters [1]. It seemed to the writer that this omission greatly reduced the value of the work on this hypothesis and its application to soil problems; an attempt is made in the present paper to fill this gap in our knowledge.

The movement of iron as complex organic ions has also been proposed by some workers, who assume that simple organic acids produced during decomposition of organic matter bring iron into solution in complex forms and carry it downwards. Jones and Wilcox [9] suggested that the iron is precipitated in the B horizon through the formation of basic salts, whereas Gallagher [10] suggested that the precipitation takes place through the decomposition of the organic part of the complex. Very little is known of the chemical nature of the decomposition products of plant and animal residues, but the presence of simple organic acids, capable of forming complex iron salts, may be postulated under certain conditions. It is difficult to establish the presence of complex organic anions containing iron in soils, but if it can be shown that such complexes would be precipitated in the B horizon of a podzol and not in the A horizon, this would at least be consistent with the possibility that iron may move in this way.

From the above considerations it was decided to study

(i) the mutual coagulation and peptization of iron-oxide sol and humus sols with special reference to concentration and pH values;
(ii) the factors responsible for the precipitation of iron oxides in B horizons of podzol soils.

The Coagulation and Peptization of Iron-oxide and Humus Sols

Humus

The chemical composition and the physico-chemical properties of humus depend on the source from which it is obtained and on the methods of extraction. A variety of humus extracts was therefore prepared in the following ways:

1. *Water-soluble peat.* Humus was obtained from an acid peat by washing 200 mg. of peat with N/20 hydrochloric acid and then with water till the extract was free from chloride. The extracted peat was treated with 2 litres of water, shaken occasionally for 2 weeks, and filtered.

2. *Alkali-soluble humus.* Humus was extracted from an acid heath soil by 2 per cent. sodium hydroxide, filtered, and dialysed.

3. *Acid-soluble humus.* The sodium-hydroxide extract of the heath soil was treated with 5 per cent. hydrochloric acid to give a final pH value of 3. The mixture was filtered and the filtrate dialysed till free from chloride.

4. *Water-soluble fen humus.* 25 gm. of an alkaline fen soil were washed with 500 c.c. of normal sodium chloride and the humus extracted by water. The humus was dialysed till free from chloride.

5. *Oxalic-acid-soluble humus.* 20 gm. of the B horizon of a podzol soil were shaken for an hour with 20 c.c. of normal oxalic acid. The humus in the extract was precipitated by adding hydrochloric acid and then washed with 5 per cent. hydrochloric acid until it was free from sesquioxides. The precipitate was dispersed in water after freeing it from chloride by dialysis.

TABLE I

The Amounts of Humus and Iron in mg. per c.c. in Different Extracts, and the pH of the Extracts

Type of Humus	*Humus*	*Iron*	*pH*
Water-soluble peat . .	0·24	0·008	4·76
Acid-soluble . . .	0·25	0·01	5·10
Water-soluble fen . .	0·80	0·03	5·46
Alkali-soluble . . .	0·48	0·04	5·90
Oxalic-acid-soluble . .	0·63	traces	3·83

Iron was estimated by α-α dipyridil after oxidation of humus with hydrogen peroxide in presence of sulphuric acid.

Carbon was estimated by oxidation with potassium permanganate.

Iron-oxide sol was prepared by the method of Neidle and Barab [11].

Mutual coagulation and peptization. To measured volumes (20 c.c., 40 c.c., 80 c.c.) containing 4 mgm. of ferric oxide varying amounts of humus extracts up to 2·5 c.c. were added. The final concentrations of ferric oxide varied from 49 to 50 p.p.m., 95 to 100 p.p.m., and 180 to 200 p.p.m. The mixtures were shaken for a minute and allowed to stand for 24 hours. Iron was estimated in the supernatant liquid.

Flocculation value. 20 c.c. lots of a sol containing 100 p.p.m. of ferric oxide were transferred to a series of test-tubes and 20 c.c. of salt solution containing varying amounts of salt were added and the tubes were shaken uniformly. Flocculation was measured after 24 hours.

Experimental results

In preliminary experiments it was observed that the concentration of humus did not affect the coagulation or peptization of iron-oxide sol, but that, on the other hand, the concentration of iron oxide markedly changed the quantity of humus necessary for coagulation and peptization. Since the soil solution rarely contains more than 100 p.p.m. of ferric oxide, and in order to measure iron without appreciable error, three concentrations, 200 p.p.m., 100 p.p.m., and 50 p.p.m. of iron oxide, were taken to study the effect of concentration on mutual coagulation and peptization. Typical results are illustrated in Fig. 1.

With different humus extracts the curves remained similar in shape to those in Fig. 1, although the amounts of humus required for coagulation and peptization varied considerably. The curves in Fig. 1 demonstrate that the points at which half the iron is coagulated or peptized, respectively, are sensitive to small alterations in amounts of added humus, but

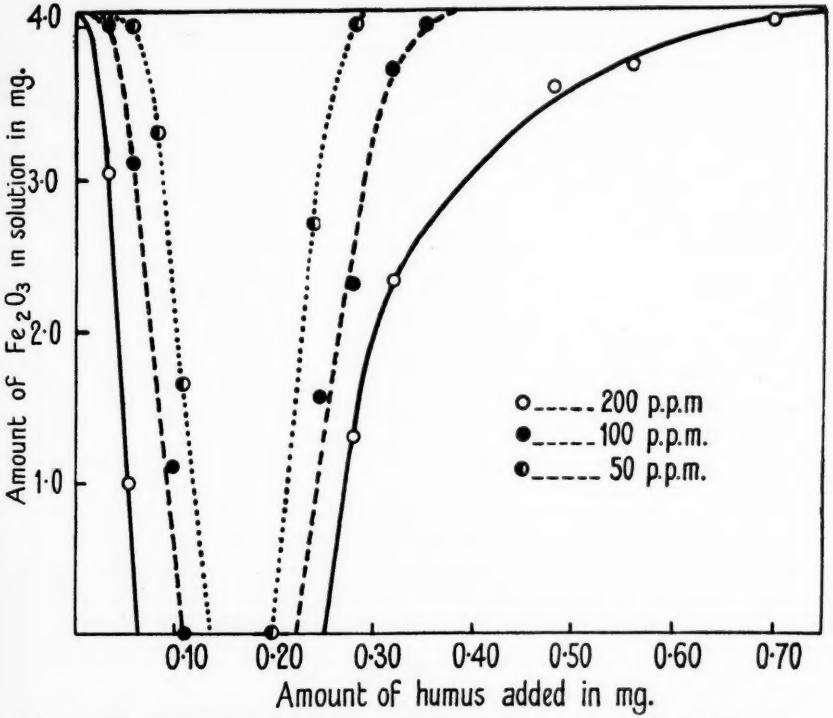

FIG. 1. The mutual coagulation and peptization of Fe_2O_3 sol. by water-soluble peat humus.

that full coagulation or full peptization can occur over a wide range in humus concentration. For characterizing the effectiveness of various humus extracts on the coagulation and peptization of different concentrations of iron-oxide sols half-coagulation and half-peptization values are given in Table 2.

It will be seen from Table 2 that

1. The amounts of humus necessary to coagulate and peptize ferric sols vary with the kind of humus sols. Thus for all three concentrations of ferric-oxide sol the order of effectiveness of coagulation and of peptization is water-soluble peat humus > acid-soluble humus > water-soluble fen humus > alkali-soluble humus > oxalic-acid-soluble humus.

2. For all humus sols larger amounts are needed to coagulate the less concentrated ferric-oxide sols.
3. In contrast to coagulation it was found that the lower the concentration of iron-oxide sol, the smaller is the amount of humus necessary for peptization.

TABLE 2

Amounts of Humus per 100 Fe_2O_3 *for Half-coagulation and Half-peptization*

Type of humus	*Half-coagulation p.p.m.* Fe_2O_3 *taken*				*Half-peptization p.p.m.* Fe_2O_3 *taken*				*Ratio* $\frac{1}{2}$ *coag.* $\frac{1}{2}$ *pept.*
	200	*100*	*50*	*Mean*	*200*	*100*	*50*	*Mean*	*mean*
Water-soluble peat .	1·0	1·6	2·4	1·7	7·1	5·3	5·4	6·3	0·27
Acid-soluble . .	2·9	3·4	4·1	3·5	9·5	8·8	8·0	8·8	0·40
Water-soluble fen .	3·6	3·8	4·2	3·9	11·8	9·7	8·8	10·1	0·39
Alkali-soluble . .	4·6	5·1	6·1	5·3	14·9	13·6	12·8	13·8	0·38
Oxalic-acid-soluble .	4·8	6·0	7·0	5·9	15·5	14·0	12·8	14·1	0·40
Mean . . .	3·4	4·0	4·8	..	11·8	10·5	9·6	..	..

Half-peptization is obtained when the ratio of carbon to iron atoms is from 0·24 to 0·54 for the different humus extracts. Each atom of carbon in humus is able to peptize from 2 to 4 atoms of iron in the coagulated mixture of ferric-oxide sol and humus.

The data also show that ratios of the mean for half-coagulation to the mean for half-peptization are of the same order for all humus sols except the peat extract. The peculiar behaviour of peat extract may be due to the presence of some simple organic salts in the undialysed peat extract. A filtered peat extract passed through the dialyser in other tests.

TABLE 3

Mean Values for Half-coagulation and Half-peptization

Type of humus	*P.p.m.* Fe_2O_3			
	200	*100*	*50*	*Mean*
Water-soluble peat . .	4·0	4·0	3·9	4·0
Acid-soluble . . .	6·2	6·1	6·0	6·1
Water-soluble fen . .	8·2	6·8	6·5	7·2
Alkali-soluble . . .	9·8	9·4	9·4	9·5
Oxalic-acid-soluble . .	10·2	10·0	9·9	10·0
Mean	7·6	7·2	7·2	..

The data in Table 3 show that the mean of the half-coagulation and half-peptization values does not depend on the concentration of iron-oxide sol, though it varies between the different humus extracts. The ratios of carbon to iron atoms for the mean values given in Table 3 are 0·16, 0·24, 0·28, 0·37, and 0·39 for the different humus extracts.

Flocculation of iron-oxide sol containing various amounts of humus

Amounts of humus (peat extract) to give 1, 2, 8, 9, 10, 11, 13, and 15 parts per 100 parts ferric oxide were added to ferric-oxide sols (approximately 100 p.p.m.) and the volume made up so that the concentration of ferric oxide was 100 p.p.m. Some of the mixed sols were partially coagulated and partially peptized. In such cases the supernatent liquid after settling of the coagulum was taken for measuring flocculation.

The results of the flocculation tests are given in Table 4.

TABLE 4

Concentration of Salt Solution in m.e. per litre required for Complete Flocculation of an Equal Volume of Fe_2O_3 *Sol (pH 5·9) or of Supernatant Liquid from Sols partly coagulated or peptized by Peat Extract (pH 4·76)*

Amount of humus per 100 Fe_2O_3	*State of mixture*	KCl	K_2SO_4	$CaCl_2$
0	..	9·0	0·25	10·5
1	Partially coagulated	5·5	0·13	5·5
2	,, ,,	2·0	0·10	2·1
8	Partially peptized	3·0	5·5	0·30
9	,, ,,	4·0	8·5	0·45
10	Fully peptized	5·8	11·0	0·50
11	,, ,,	9·3	18·0	0·65
12	,, ,,	22·0	35·0	1·0
13	,, ,,	45·5	62·5	1·7

It will be seen from Table 4 that

1. With ferric-oxide sol without humus almost equivalent amounts of potassium chloride and calcium chloride and only very small amounts of potassium sulphate are required for flocculation.
2. The partially coagulated ferric-oxide sols prepared with 1 per cent. and 2 per cent. humus required less electrolyte for flocculation than ferric-oxide sols without humus. The charges of the sols were still positive; SO_4^{--} ion was more effective than Cl^- ion.
3. In sols prepared with 8 per cent. humus SO_4^{--} ion became ineffective and Ca^{++} ion effective in flocculation, showing that the sol has changed to a negative one.
4. With larger amounts of humus the stability of the sol as a negative colloid increased considerably.
5. Whereas the ferric-oxide sol without humus required 10·5 m.e. of calcium chloride for flocculation, the fully peptized negative sol required only 0·5 m.e.

So far a ferric-oxide sol of pH 5·9 had been used, but as the movement of iron in podzolization takes place under more acid conditions, ferric-oxide sols of different pH values were prepared by adding different amounts of dilute hydrochloric acid to the pure sol. The mutual coagulation and peptization of these sols by peat-humus extracts gave results illustrated in Fig. 2.

It will be seen from Fig. 2 that the lower the pH the higher is the amount of humus required for coagulation and peptization. Thus, half-coagulation occurs with 2·8 per cent. humus at pH 5·9, whereas 6·5 per

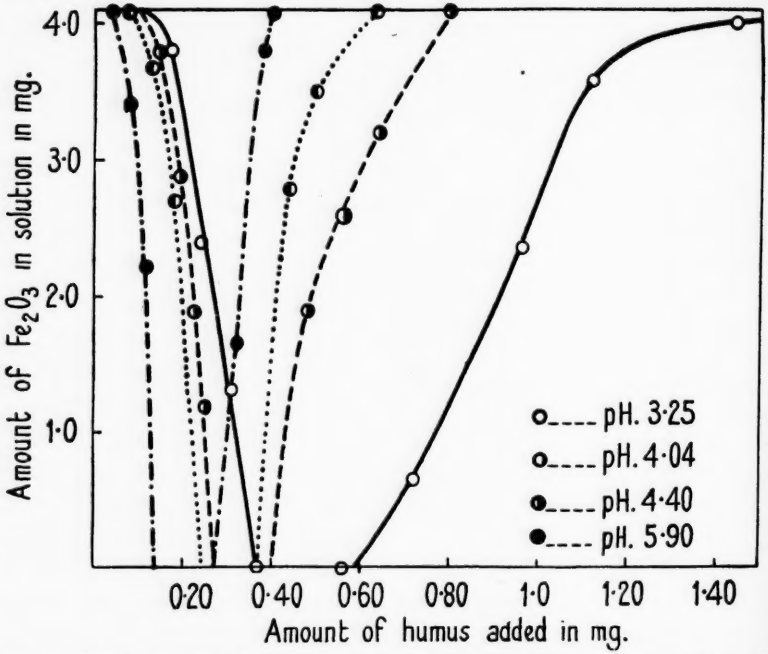

FIG. 2. Effect of pH of the Fe_2O_3 sol on mutual coagulation and peptization of Fe_2O_3 sol by water-soluble peat.

cent. humus is required for half-coagulation at pH 3·25. Similarly 6·8 per cent. humus is required for half-peptization at pH 5·9 and 22·4 per cent. at pH 3·25.

II. *The Precipitation of Iron in Podzol Soils*

It was observed in the previous section that whereas 10 m.e. of Ca^{++} were required to flocculate pure ferric-oxide sol, only 0·5 m.e. of Ca^{++} was required for ferric-oxide sol fully peptized by humus. This result seems to substantiate a common view that iron is precipitated in the B horizon by divalent cations. In order to test this experimentally, soils of the B and C horizons of a sandy podzol were perfused for 3 days with a sol containing 100 p.p.m. of ferric oxide and 10 p.p.m. of humus (peat extract) by the method of Lees [12]. There was practically no adsorption of iron by the soils.

In this experiment the soils may not have contained sufficient calcium to flocculate the sol. In order to test this point a mineral soil was leached with N/20 hydrochloric acid, washed with water, saturated to different degrees with lime-water, shaken, and dried.

As it was not possible, owing to the clayey nature of these soils, to perfuse them by the method of Lees, adsorption was measured by adding 50 c.c. of humus-protected ferric-oxide sol to 1 gm. of treated soil. The mixture was shaken and aerated for 48 hours by passing air through it and then allowed to stand for 24 hours. Iron was estimated in the supernatant liquid.

TABLE 5

The pH and Amount of Lime in Treated Soil

	Ca *present* *m.e. per 100 gm.*	*pH*
A	0	4·33
B	2·2	4·81
C	3·6	5·10
D	5·4	5·50
E	7·2	6·25
F	8·6	6·80
G	10·0	7·28

There was no adsorption of iron in any case. When as little as 1 c.c. of N/100 calcium chloride was added to the flasks, iron was precipitated in all cases. The much larger quantities of calcium in the exchangeable form in the soils were ineffective in precipitating iron. These results therefore fail to support the general assumption that the precipitation of iron in podzol B horizons is due to flocculation by the divalent cations present in the exchangeable form.

TABLE 6

Iron Adsorption from Organic Salts expressed as Percentage of Added Iron adsorbed by 1 gm. of Soil from 50 c.c. of Solution containing 50 p.p.m. of Fe_2O_3

Soil	*Horizon*	*pH*	*Ferric malate*	*Ferric tartrate*	*Ferric citrate*	*Ferric ammonium citrate*
C 9. Podzolic soil from Scotland	B	5·00	60	49	41	20
	C	5·02	58	44	40	15
G 7. Humus podzol from Scotland	B_1	4·88	54	58	41	18
	B_2	4·97	21	16	11	15
R 3. Humus podzol from Scotland	B_1	4·33	50	34	33	15
	B_2	5·00	33	17	7	13
Soils treated with lime						
A		4·33	27	16	14	18
C		5·10	25	20	11	8
E		6·25	23	25	14	7
G		7·28	32	25	14	10

The possibility of the movement of iron as complex salts of iron and organic acids has been suggested by some workers. In order to test how these salts are precipitated in B horizons of podzol soils three podzolic

soils and soils saturated to different degrees with calcium were used to measure the adsorption of iron from complex salts of iron and organic acids. The method of estimation was similar to those for humus-protected ferric-oxide sol.

Table 6 gives results for the adsorption of iron by soils from iron organic salts.

The results show that the adsorption of iron from salt solutions is not dependent either on pH or on the amount of divalent cations. Thus the B_2 horizon of R_3 with pH 5·0 adsorbed 33 per cent., whereas the B_1 horizon of R_3 with pH 4·33 adsorbed 50 per cent. of the amount added as ferric malate. Similarly a soil having no exchangeable calcium or other divalent cations and a pH value of 4·33 adsorbed 23 per cent., whereas the same soil saturated with calcium and containing 10 m.e. calcium per 100 gm. adsorbed only 32 per cent. of the amount added.

Discussion

The movement of iron from the A horizon and its precipitation in the B horizon are fundamental characteristics of podzol profiles. A discussion on the likely modes of movement of iron in podzol soils shows that iron may move as

(*a*) a negatively charged humus-protected iron-oxide sol, or

(*b*) a complex organic ion.

Some workers, e.g. Gallagher and Walsh [13] and Winters [1], have raised the question whether the amount of humus in the soil solution can be sufficient to peptize the iron oxide. Data given by Aarnio [5, 6] and Winters [1] suggested that the amount of humus required for peptization may exceed 2·5 times the amount of ferric oxide. These workers, however, did not pay attention to the effect of the concentration and reaction of the sols. In the present study of the mutual coagulation and peptization of iron-oxide sol by humus sol it has been found that the amounts of humus necessary to peptize iron-oxide sol vary considerably with the source of humus and the concentration and pH of the iron-oxide sol. Over a wide range of concentrations of iron-oxide sol full precipitation occurred with about 7 parts of humus per 100 parts of ferric oxide. The amounts of humus required varied according to the form of humus, but the ratio of humus to ferric oxide was constant for each kind of humus over a wide range of concentrations. The amounts of humus required to peptize one-half of the coagulated complex of humus and iron oxide was on the average about 10 parts of humus per 100 parts of ferric oxide. The amount of humus required is therefore much less than that suggested by many of the earlier workers.

The lysimeter studies of podzol horizons by Mattson and Koutler-Andersson [2] and Joffe [14] show that the concentration of iron oxide in the soil solution is always below 100 p.p.m. and that the amounts of humus are always considerably higher than of the sesquioxides.

From the results of the present investigation it can be said that the amount of humus necessary for the full peptization of an iron-oxide sol

having 100 p.p.m. of iron oxide and a pH value near 4·0 will not be more than 30–40 per cent. of the amount of iron oxide. Relatively less humus will be required for more dilute iron-oxide sols. It is therefore evident that any iron-oxide sol formed by weathering in the upper horizons of podzols should be fully peptized by the humus in soil solution and carried down the profile by percolating water.

The precipitation of iron in the B horizon of podzol soils is generally believed to be due to the colloidal flocculation of humus-protected iron-oxide sol or the chemical precipitation of complex salts of iron and organic acids. In order to test these views samples of B and C horizons of a few podzolic soils and also a soil saturated with different degrees of calcium were either perfused or shaken with a humus-protected iron-oxide sol, but practically no adsorption took place in any case. These results show that exchangeable calcium alone is not sufficient to flocculate humus-protected iron-oxide sol.

The amount of adsorption of iron by sols from various complex salts of iron and organic acids also showed that the adsorption of iron is not influenced by the pH of soils or the amount of exchangeable calcium. These results suggest that the precipitation of iron in the B horizons of podzol soils is not due either to colloidal flocculation of a humus-protected iron-oxide sol or to the chemical precipitation of complex salts of iron and organic acids. It is therefore necessary to consider other mechanisms. It is possible that the processes governing the precipitation are of a microbiological rather than colloidal or chemical nature. In this connexion it may be pointed out that Harder [15], in his work on iron bacteria, showed that the precipitation of iron from complex salts of iron and organic acids is a microbiological process. Recently Albrecht [16] has suggested that the development of a gley horizon might be microbiological in origin. Roots of trees and other plants often reach to and sometimes are concentrated near the upper layer of the B horizon. By their decay they would supply the necessary organic matter and other nutrients to support an active soil microflora.

Summary

Consideration of the mechanisms proposed for the movement of iron in podzol profiles suggested that the iron moved either as a negatively charged humus-protected iron-oxide sol or as a complex organic ion.

In a study of the mutual coagulation and peptization of iron-oxide and humus sols it was found that the amount of humus necessary for the full peptization of a sol containing 100 parts of iron oxide per million parts of solution with a pH value around 4·0 was not more than about one-third the amount of iron oxide. This is a much smaller ratio of humus to iron oxide than was formerly believed to be necessary.

No evidence could be found to support the view that precipitation of iron from humus-protected sols is effected by exchangeable calcium in the B horizons of podzols or that the adsorption of iron from complex salts of organic acids is influenced by the pH or amounts of exchangeable bases present in the soil. It therefore appears necessary to postulate a microbiological mechanism for the precipitation of iron.

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